Trends in the Proton NMR Spectra of Some Amine-Haloboranes: Steric Effects

By

WILLIAM HOWARD MYERS

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to Barbara

what has been
is exceeded only by
what is yet to be

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TABLE OF CONTENTS

Page

ACKNOWLEDGMENTS iii

LIST OF TABLES viii

LIST OF FIGURES ix

ABSTRACT xii

CHAPTER I. INTRODUCTION 1

CHAPTER II. MATERIALS AND PROCEDURES 17

Materials 17

Apparatus and Methods 17

Computer Analysis of ^{1}H NMR Spectra of Diethylamine-Haloboranes 18

CHAPTER III. SYNTHESES AND REACTIONS 22

Preparation of Triethylamine-Haloboranes 23

Reaction of triethylamine-borane and chlorine 23

Reaction of triethylamine-borane and bromine 24

Reaction of triethylamine-borane and iodine 26

Reaction of triethylamine and boron trifluoride-etherate . . . 29

Preparation of Dimethylamine-Haloboranes 29

Synthesis of dimethylamine-mono- and dichloroborane . . . 29

Synthesis of dimethylamine-trichloroborane 29

Reaction of dimethylamine-borane and bromine 30

Synthesis of dimethylamine-tribromoborane 33

Reaction of dimethylamine-borane and iodine 34

Page

Synthesis of dimethylamine-triiodoborane 37

Synthesis of dimethylamine-trifluoroborane 38

Reaction of Dimethylamine and Boron Trihalides 42

Reaction of dimethylamine and boron trichloride 42

Synthesis of bis-(dimethylamine)-boronium chloride . . 45

Synthesis of bis-(dimethylamine)-dichloroboronium chloride 47

Reaction of bis-(dimethylamine)-dichloroboronium chloride and boron trichloride 47

Reaction of dimethylamine and boron tribromide 50

Preparation of Diethylamine-Haloboranes 55

Synthesis of diethylamine-borane 55

Synthesis of diethylamine-monochloroborane 55

Synthesis of diethylamine-dichloroborane 58

Synthesis of diethylamine-trichloroborane 61

Reaction of diethylamine-borane and hydrogen bromide . 66

Reaction of diethylamine-borane and bromine 66

Synthesis of diethylamine-tribromoborane 69

Synthesis of diethylamine-monoiodoborane 69

Reaction of diethylamine-borane and iodine 73

Reaction of diethylamine and boron trifluoride-etherate . 76

Reaction of N-Deuterodimethylamine-Borane with Various Halogenating Agents 76

Synthesis of N-deuterodimethylamine-borane 76

Reaction of N-deuterodimethylamine-borane and chlorine 78

Page

Reaction of N-deuterodimethylamine-borane and bromine 78

Reaction of N-deuterodimethylamine-borane and iodine . . 79

Reaction of N-deuterodimethylamine-borane and hydrogen chloride 79

Reaction of N-deuterodimethylamine-borane with hydrogen chloride and chlorine 80

Reaction of N-deuterodimethylamine-borane with deuterium chloride and chlorine 80

Reaction of N-deuterodimethylamine-borane and hydrogen chloride at low temperature and the synthesis of N-deuterodimethylamine-mono- and dichloroborane . . . 81

Reaction of N-deuterodimethylamine-monochloroborane and chlorine 83

Reaction of N-deuterodimethylamine-dichloroborane and chlorine 83

Reaction of N-deuterodimethylamine-borane and chlorine at low temperature 84

Reaction of N-deuterodimethylamine-trichloroborane and hydrogen chloride 84

Reaction of N-deuterodimethylamine-trichloroborane with hydrogen chloride and chlorine 85

Reaction of dimethylamine-trichloroborane and deuterium chloride 86

CHAPTER IV. DISCUSSION 92

Halogenation of Amine-Boranes 92

Reaction of Dimethylamine and Boron Trihalides 95

Reaction of N-Deuterodimethylamine-Borane with Various Halogenating Agents 102

Page

General ^{1}H NMR Results 110

Possible Explanations of the Effect of Boron-Attached Halogens on the NMR Shifts of Alkyl Protons in Donor Groups Attached to Boron 114

Diethylamine-Haloborane ^{1}H NMR Results 123

Further Comments 129

Comments on the Work of Rothgery and Hohnstedt . . . 129

Comments on the Solvent Dependence of NMR Spectra of Diethylamine-Haloboranes 132

Comments on the Temperature Dependence of NMR Spectra of Amine-Haloboranes 133

BIBLIOGRAPHY 136

BIOGRAPHICAL SKETCH 142

LIST OF TABLES

Table No.	Title	Page
I	Infrared Data for Some Amine-Haloboranes	87
II	^{1}H NMR Data for Haloborane Adducts of $(CH_3)_3N$ . . . . and $(CH_3)_2NH$	89
III	^{1}H NMR Data for Haloborane Adducts of $(CH_3CH_2)_3N$ . . .	90
IV	^{1}H NMR Data for Haloborane Adducts of $(CH_3CH_2)_2NH$ . .	91

LIST OF FIGURES

Figure		Page
1.	Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_3NBCl_3$	25
2.	Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_3NBBr_3$	27
3.	Infrared spectrum of $(CH_3)_2NHBCl_3$	31
4.	^1H nmr spectrum of $(CH_3)_2NHBCl_3$	32
5.	Infrared spectrum of $(CH_3)_2NHBBr_3$	35
6.	^1H nmr spectrum of $(CH_3)_2NHBBr_3$	36
7.	Infrared spectrum of $(CH_3)_2NHBI_3$	39
8.	^1H nmr spectrum of $(CH_3)_2NHBI_3$	40
9.	Infrared spectrum of $(CH_3)_2NHBF_3$	41
10.	^1H nmr spectrum of $(CH_3)_2NHBF_3$	43
11.	Infrared spectrum of fraction (A) from the reaction of $(CH_3)_2NH$ and BCl_3	46
12.	Infrared spectrum of $[(CH_3)_2NH]_2BH_2^+Cl^-$	48
13.	Infrared spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$	49
14.	Infrared spectrum of $[(CH_3)_2NH]_2BCl_2^+BCl_4^-$	51
15.	Infrared spectrum of fraction (A) from the reaction of $(CH_3)_2NH$ and BBr_3	54
16.	Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBH_3$	56
17.	Infrared spectrum of $(CH_3CH_2)_3NHBH_3$	57
18.	Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBH_2Cl$	59
19.	Infrared spectrum of $(CH_3CH_2)_2NHBH_2Cl$	60

Figure | Page

20. Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBHCl_2$. 62

21. Infrared spectrum of $(CH_3CH_2)_2NHBHCl_2$ 63

22. Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBCl_3$. . 64

23. Infrared spectrum of $(CH_3CH_2)_2NHBCl_3$ 65

24. Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBH_2Br$. 67

25. Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBHBr_2$. 68

26. Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBBr_3$. . 70

27. Infrared spectrum of $(CH_3CH_2)_2NHBBr_3$ 71

28. Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBH_2I$ . . 72

29. Infrared spectrum of $(CH_3CH_2)_2NHBH_2I$ 74

30. Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBHI_2$ . . 75

31. Methylene region of the ^1H nmr spectrum of $(CH_3CH_2)_2NHBF_3$ . . 77

32. Chemical shift of methyl protons in haloborane adducts of $(CH_3)_2NH$ and $(CH_3)_3N$ as a function of extent of halogen substitution on boron 111

33. Chemical shift of methyl and methylene protons in haloborane adducts of $(CH_3CH_2)_2NH$ and $(CH_3CH_2)_3N$ as a function of extent of halogen substitution on boron 113

34. Sketch of approximate bond lengths, bond angles, and van der Waals' radii for an H-C-N-B-X system (X = Cl, Br, I) showing the potential for severe overcrowding 121

35. Chemical shift of non-equivalent methylene protons in haloborane adducts of $(CH_3CH_2)_2NH$ as a function of extent of halogen substitution on boron 124

36. Newman projections showing similarity between CH_3CH_2CXYZ and $CH_3CH_2N(H)(Et)(BXY_2)$ 125

Figure | Page

37. Newman projections showing rotameric isomers of $(CH_3CH_2)_2NHBXY_2$ (with torsional preferences) 128

38. Newman projections of two rotameric forms of $CH_3CH_2OC(O)CH_2N(H)(CH_3)\cdot BCl_3$ 131

39. Newman prejections showing possible non-equivalence of methyl groups in trimethylamine-haloboranes produced by hindered rotation at low temperature 134

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TRENDS IN THE PROTON NMR SPECTRA OF SOME
AMINE-HALOBORANES: STERIC EFFECTS

By

William Howard Myers

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Chairman: Professor G.E. Ryschkewitsch
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Borane adducts of triethylamine, dimethylamine, and diethylamine were halogenated using free halogens or hydrogen halides, and the proton nmr spectra of these amine-haloborane adducts were obtained. Tbe resonances of these adducts and of the haloborane adducts of trimethylamine showed a shift to lower field with increased size of halogen or with increased number of halogens on boron. This shift to lower field had been previously attributed to inductive effects, but in this work it was shown that the shift to lower field was due to steric interaction between halogens on boron and alkyl groups on nitrogen.

Proton nmr spectra for diethylamine-haloboranes were complex and showed patterns attributable to non-equivalent methylene protons. Computer analyses of the spectra allowed assignments consistent witb preferred rotational configurations.

The reactions between the secondary amine, dimethylamine, and three boron trihalides were examined in detail. Dimethylamine and boron trifluoride

reacted to produce the 1:1 adduct dimethylamine-boron trifluoride. Dimethylamine reacted with boron trichloride or boron tribromide to produce mixtures of both the 1:1 adduct and bis-(dimethylamine)-dihaloboronium tetrahaloborate salts. In order to obtain pure 1:1 adduct, it was necessary to take advantage of the low solubility of the boronium salts in methylene chloride or to directly halogenate dimethylamine-borane.

During the reaction of N-deuterodimethylamine-borane with chlorine, considerable exchange of hydrogen for deuterium on nitrogen occurred. An extensive investigation of the halogenation reactions of N-deuterodimethylamine-borane indicated that the exchange process occured only via the loss of deuterium chloride from a molecule activated as a result of halogenation.

CHAPTER I

INTRODUCTION

In the last decade, a variety of research techniques have been used to examine the relative acid character of various boranes and boron halides. On the basis of electronegativity and relative steric requirements of the halogens, the accepted order of acid strength[1] had been $BF_3 > BCl_3 > BBr_3$, but the evidence presented in these later articles indicates the reverse order to be correct.

Laubengayer and Sears[2] were the first to suggest that BF_3 is not the strongest acid of the boron trihalide series, as the result of a calorimetric study of the formation of the BF_3 and BCl_3 adducts of acetonitrile. In a later article, Miller and Onyszchuk[3] added to this work with a calormetric examination of the formation of the BBr_3 adduct of acetonitrile. In a similar study, Brown and Holmes[4] made calorimetric measurements on the formation of pyridine-boron trihalide adducts, which indicated an order of acid strength of $BF_3 < BCl_3 \leq BBr_3$.

Stimulated by this new evidence, Cotton and Leto[5] performed molecular orbital calculations of the reorganization energies involved in the formation of donor-acceptor molecules by boron trihalides. The theoretical evidence showed that the major hindrance to adduct formation for a boron trihalide involved the break-up of π-bonding between boron and the halogens, and thus that the order of acid strength was determined by relative extent of π-bonding rather than by relative electronegativity or relative steric bulk. That is, BF_3 is the poorest acid of the series because it has the most π-bonding to break up.

Additional support came from the work of Bax, Katritzky, and Sutton,[6] who determined the dipole moments of boron trihalide and borane (BH_3) adducts of trimethylamine and pyridine.

In two related articles,[7,8] Onyszchuk and others reported on a study of the gas-phase displacement reactions of boron trihalides from their trimethylamine adducts. The order of acid strength was shown, unambiguously, to be $BBr_3 > BCl_3 > BF_3 > 1/2\,(B_2H_6)$. Coyle[9] showed that this displacement can occur with or without B-N bond cleavage.

In the recent literature, two articles have appeared giving structural evidence which confirms this order of acid strengths. Ibers[10] reported the X-ray structure of $CH_3CN \cdot BF_3$ and $CH_3CN \cdot BCl_3$. The B-N bond length shortens by 0.07 Å going from the BF_3 to the BCl_3 adduct, implying a stronger B-N bond in the BCl_3 adduct. Bryan and Kuezkowski[11] reported on the B-N bond length in $(CH_3)_3NBF_3$, as determined from the microwave spectrum of the compound, and the complete crystal structures of the other $(CH_3)_3NBX_3$ adducts (X = Cl, Br, I) are to be published by Taylor.[12] In addition Bryan and Kuczkowski[11] reported a B-N bond length for $(CH_3)_3NBH_3$, as determined by Schirdewahn[13] from the microwave spectrum of the compound. These bond lengths are given below:

Compound	Bond length (Å)
CH_3CNBF_3	1.630 (± 0.004)
CH_3CNBCl_3	1.562 (± 0.008)
$(CH_3)_3NBH_3$	1.65 (± 0.02)
$(CH_3)_3NBF_3$	1.636 (± 0.004)

Compound	Bond length (Å)
$(CH_3)_3NBCl_3$	1.610 (± 0.006)
$(CH_3)_3NBBr_3$	1.603 (± 0.02)
$(CH_3)_3NBI_3$	1.584 (± 0.025)

The B-N bond length is seen to become shorter as one goes from BF_3 to BI_3 as the coordinating acid. This is consistent with the strength of interaction (i.e., acid strength of BX_3 towards a given donor) increasing in the order $BF_3 < BCl_3 < BBr_3 < BI_3$. However, on the basis of relative base strengths, one would expect the B-N bond to be shorter for a given $(CH_3)_3NBX_3$ adduct than for a corresponding CH_3CNBX_3 adduct. The data above show the B-N bond length to be about the same for the two BF_3 adducts, and significantly shorter for the CH_3CNBCl_3 complex compared to the $(CH_3)_3NBCl_3$ complex. One possible rationalization for this anomaly lies in the fact that nitrogen in CH_3CN uses an sp hybrid orbital to bond to boron while nitrogen in $(CH_3)_3N$ uses an sp^3 hybrid orbital. A consideration of some simple organic molecules predicts a shortening of 0.05 to 0.08 Å for a change from sp^3 to sp hybridization for one carbon in a C-C single bond. Thus, CH_3CNBF_3 and $(CH_3)_3NBF_3$ would have similar B-N bond strengths only if the B-N bond in CH_3CNBF_3 were at least 0.05Å shorter. (Valence force constants were determined for the B-N bond in $(CH_3)_3NBF_3$ by Clippard[14] and in CH_3CNBF_3 by Swanson and Shriver.[15] The values are 3.53 mdynes/Å [$(CH_3)_3NBF_3$] and 2.5 mdynes/Å (CH_3CNBF_3), demonstrating that the interaction in $(CH_3)_3NBF_3$ is indeed much stronger.) One would also have expected the change from BF_3 to BCl_3 to have affected the two adducts similarly, yet the B-N bond in the CH_3CNBCl_3 adduct is shortened

by 0.04 Å more than the B-N bond in $(CH_3)_3NBCl_3$. One might conclude that steric interaction (F-strain) in $(CH_3)_3NBCl_3$ precludes the B-N bond from shortening as much as expected. One should note that, within experimental error, the B-N bond length is the same in the $(CH_3)_3N$ adducts with BCl_3, BBr_3, and BI_3, although bond shortening would have been expected. This is also consistent with steric interaction (F-strain) interfering with B-N bonding. Taylor[12] comments that these three adducts are sterically quite crowded. In fact, a comparison of the intramolecular non-bonded distances with the sum of the van der Waals radii shows that the X-CH_3 distance is shortened by about 0.63 Å; this implies a considerable interaction.

Having determined with good confidence that the order of acidity in the boron trihalides was $BF_3 < BCl_3 < BBr_3 < BI_3$, several attempts have been made to correlate spectral properties of donor-acceptor complexes with acidity. The basic tenets for three major areas of work* are set down below, with references to pertinent articles:

1. Infrared Spectral Shifts.[14-20] These correlations are based on the effect of the acceptor group on electron density in the donor group. For example, coordination of an acid group to a carbonyl group removes electron density from

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* A fourth type of spectroscopic investigation of donor-acceptor compounds has recently been reported by Lanthier and Miller.[16] They examined the mass spectra of trimethylamine adducts of the boron trihalides and some mixed trihalides and found that the results could be explained in terms of relative acceptor strength of the boron trihalides and borane towards trimethylamine. The results are consistent with the Lewis acidity increasing with size of the halogen, and evidence is presented which indicates decreasing boron-halogen bond strength with increasing size of halogen. This last trend is discussed in terms of "residual π-bonding" between boron and halogen in the amine-borane molecule. (For a full discussion of this last point, see Brown, Drago, and Bolles.[17])

the oxygen, thus polarizing the C-O bond. The electrons in the π-system would be more localized on oxygen, and the C-O bond strength would decrease. Another way to express this idea is to say that there is an increased contribution of a resonance form which has the π-bonding electrons localized on oxygen, and the formal positive charge localized on carbon. The lowering of the C-O bond strength would cause the C-O stretch to shift to lower frequency, and the magnitude of the shift is a measure of the strength of interaction, i.e., a measure of the acid strength of the acceptor group. Of course, the real variable one is attempting to evaluate in this manner is the force constant of the bond, and one must be careful to establish that the bond whose force constant is to be qualitatively examined by this method has its stretching motions isolated from other molecular vibrations. If the stretching motion is strongly coupled to other motions in the molecule, problems in interpretation may arise. A case in point is the B-N bond in CH_3CNBX_3 adducts, which is highly coupled to other motions in the molecule. This system has been examined by Beattie and Gilson,[21] Purcell and Drago,[22] and Swanson and Shriver.[15]

An interesting correlation is reported by Coyle and Stone[23] for donor strength in adducts containing B-H bonds. This correlation is based on Cotton and Leto's argument of reorganization energy,[5] and suggests that the more stable an adduct is, the more tetrahedral the groups around the donor and acceptor atoms should be. Thus, since the s character of B-H bonds in such a system would be less in a tetrahedral case (sp^3) than in a case where the acceptor moiety approaches planarity (sp^2), the B-H bond should be weaker in the more strongly bonded adduct; that is, the B-H stretch should shift to

lower frequency. The data presented by Coyle and Stone are, for the most part, consistent with this picture. However, a more general point of view would be to look at the system as a B^{+3} ion coordinated to three donor groups (X, Y, and Z) and hydride (H^-). Changes in the donor groups will affect the stretching frequency of the B-H bond in a predictable manner, namely, the more electron-releasing the donor groups become, the more electron density will be pushed onto the hydrogen, and the more the B-H stretch will shift to lower frequency. Conversely, the more electron-withdrawing the donor groups become, the more electron density will be pulled away from the hydrogen, and the more the B-H stretch will shift to higher frequency. In other words, the B-H stretching frequency should be a measure of the "hydridic character" of the boron-attached hydrogen. Thus, the B-H stretching frequency in a series of $(CH_3)_3NBHX_2$ adducts (X = Cl, Br, and I) may be explained on this basis. The values are as follows:

Compound	$\nu_{B-H}(cm^{-1})$	Reference
$(CH_3)_3NBHCl_2$	2480	24
$(CH_3)_3NBHBr_2$	2510	25
$(CH_3)_3NBHI_2$	2525	25

One may conclude that the net withdrawal of electron density by X in $(CH_3)_3NBHX_2$ is in the order Cl<Br<I. This is another indication that π-bonding effects may outweigh electronegativity effects, even in tetrahedral boron. (For a full discussion of this last point, see Brown, Drago, and Bolles.[17])

2. <u>^{11}B NMR Data.</u>[26-30] There have been two major attempts to correlate ^{11}B nmr data with acidity. Muetterties[26] was the first to suggest that $^{11}B-^{1}H$

coupling constants, in compounds containing B-H bonds, might be a measure of donor-acceptor interaction, on the basis that the value of the coupling constant is related to the amount of s-character in the boron orbital used in bonding to hydrogen. (The idea originated in the study of ^{13}C nmr data; see, for example, Gutowsky et al.[31]) One can rationalize the idea as follows. The greater the acidity of a given borane, the more easily the borane "reorganizes"[5] to tetrahedral geometry. Since the more tetrahedral the borane, the less s-character in B-H bonds (sp^3 vs. sp^2), it follows that if the $^{11}B-^{1}H$ coupling constant is directly proportional to the amount of s-character in the B-H bond, the coupling should decrease with increasing acidity. Conversely for a given borane, the greater the base strength of the donor group, the more tetrahedral the borane, thus the less the s-character and the less the coupling constant.

In practice, this concept works only for limited situations, that is, for systems in which the donor group is varied, or in which the borane group is varied within limits. A case in point where the correlation does not hold is in the case of $(CH_3)_3N$ coordinated to BH_3, BH_2Cl, and $BHCl_2$. The $^{11}B-^{1}H$ coupling constants for these three adducts are 101, 123, and 152 Hz, respectively.[24] The acidity of these groups surely increases in the order $BH_3 < BH_2Cl < BHCl_2$, but the $J_{^{11}B-^{1}H}$ values indicate the reverse order.

A rationalization of sorts is obtained by considering the various factors which affect the value of $J_{^{11}B-^{1}H}$. Grant and Litchman[32] pointed out that $J_{^{13}C-^{1}H}$ values are not only a function of relative s-character but also of effective nuclear charge at the carbon:

$$J_{obs} \propto (\text{relative s-character})^2(\text{relative effective nuclear charge})^3(J \text{ in } CH_4).$$

Thus, the correlation of J values with relative s-character works only when the relative effective nuclear charge is constant. When a system is considered in which great changes occur in effective nuclear charge at carbon, one cannot use J values as indicators of relative s-character.

In the system described above [$(CH_3)_3N$ coordinated to BH_3, BH_2Cl, and $BHCl_2$] the changes in effective nuclear charge at boron as a result of chloride substitution have apparently swamped out any effect of relative s-character. That is, increasing the effective nuclear charge at boron will increase the value of $J_{^{11}B-^{1}H}$, no matter what the effect on relative s-character of the boron orbitals used to bond to hydrogen.

The change in B-H stretching frequency in these adducts supports this argument. The frequencies[33] (symmetrical stretch) are 2260-2290 (BH_3 adduct), 2340 (BH_2Cl adduct), and 2480 ($BHCl_2$ adduct) cm^{-1}. The trend in frequencies implies a lowering of hydridic character in the order $BH_3 > BH_2Cl > BHCl_2$ which would be expected if the acidity increases in the order $BH_3 < BH_2Cl < BHCl_2$.

It should be noted that a rough correlation of structure to $J_{^{11}B-^{1}H}$ can be made for tetracoordinate boron as shown below:

Species	Approximate $J_{^{11}B-^{1}H}$ in Hz	
BH_4^-	80	
X_2BH_2, XBH_3	100	X = N, O donor
borazines, $XYBH_2$, X_2YBH	120-140	Y = Cl, Br, I
boroxines, XY_2BH	140-170	

The predominant factor would appear to be electronegativity, or, in other words, for a wide variety of compounds, $J_{^{11}B-^{1}H}$ is a function of relative effective nuclear charge at boron.

The second major attempt to correlate ^{11}B nmr data with strength of donor-acceptor interaction was based on Mooney's idea[27a-g] that the change in ^{11}B chemical shift from uncomplexed to complexed borane is a good measure of the strength of the donor-acceptor bond. Heitsch[28] directly contradicted this idea, pointing out that the order of basicity as determined by ^{11}B chemical shifts for a series of amines coordinated to BH_3, BF_3, and $B(CH_3)_3$ cannot be rationalized on the basis of any known or assumed order of complex stability. Mooney, in a review article,[29] suggested that the data Heitsch compiled might be suspect because of the solvents he used — 1, 4-dioxane and acetonitrile. In addition, Mooney sidestepped the issue by suggesting that the orders of basicity which Heitsch's data imply might actually be the true orders of base strength towards the reference acid in question.

Mooney[27a] has given ^{11}B chemical shift data for triethylamine adducts of BX_3(X = F, Cl, Br, I). Heitsch[28] gave a value for the ^{11}B chemical shift of triethylamine-boron trimethyl, and Muetterties[26] gave a value for the ^{11}B chemical shift of uncomplexed trimethylboron. These data are given below (all δ relative to external $Et_2O \cdot BF_3$):

Borane	$\delta_{^{11}B}$ of free borane	$\delta_{^{11}B}$ of Et_3N adduct	$\Delta\delta$ (after Mooney)
BF_3	-----	- 0.2	+ 9.5
BCl_3	-----	-10.0	+ 37.6
BBr_3	-----	+ 5.1	+ 45.1
BI_3	-----	+59.8	+ 53.1
$B(CH_3)_3$	-86.4	+13.6	+100.0

Thus, according to Mooney's criterion, $B(CH_3)_3$ would be a stronger acid than any BX_3 (X = halogen) toward Et_3N. This perhaps conclusively demonstrates that Mooney's criterion is not universally applicable, and thus that care should be taken in its use.

Although the work of Spielvogel[30] was not directly concerned with the question of strength of donor-acceptor interaction, it is nevertheless of such significance that it should be briefly discussed. Essentially, Spielvogel attempted to correlate ^{11}B chemical shifts with the nature of the substituents on boron. Such a correlation has been relatively successful in the study of ^{13}C shifts, and the idea that the same type of correlation exists for ^{11}B is not surprising. Briefly, the correlation works as follows. So-called "pair wise additivity parameters" are determined for possible substituent combinations. Four substituents may be grouped into <u>six</u> groups of two substituents each. For each group, a contribution to the shift is assumed, and the sum of the six contributions is a good measure of the ^{11}B chemical shift of the molecule. As an example, consider Et_3NBHBr_2. The four substituents are Et_3N (actually R_3N for an approximate calculation), H, Br, and Br. The six groups are then: [Et_3N, H], [Et_3N, Br], [Et_3N, Br], [H, Br], [H, Br], and [Br, Br]. The contributions for these groups are (in ppm from $Et_2O \cdot BF_3$):

Group	Contribution to $\delta_{^{11}B}$ (ppm)
[Et_3N, H]	-1.63
[Et_3N, Br]	-4.57
[H, Br]	+4.52
[Br, Br]	+6.27

The chemical shift is then calculated to be:

$$\delta = \Sigma[X, Y] = (-1.63) + 2(-4.57) + 2(4.52) + (6.27) = +4.54 \text{ or } \underline{4.5} \text{ ppm.}$$

In the present work, the observed value for the ^{11}B chemical shift of this compound was 2.1 ppm referred to the same standard.

In this manner Spielvogel also calculated $\delta(Et_3NBHI_2) = 39.4$ ppm, while the observed value in the present work was $\delta = 24.3$ ppm. The agreement in this second case is not so good; however in most cases the agreement between calculated and observed values for the ^{11}B chemical shifts was very good, typically with less than ± 1.0 ppm error.

3. <u>^1H NMR Data.</u>[34-38] Coyle and Stone[34] were the first to attempt to correlate ^1H nmr shifts to donor-acceptor properties and adduct stabilities. They examined a series of donor molecules (which contained $-CH_2CH_3$ groups) coordinated to BH_3, BF_3 and $B(CH_3)_3$, to see if any correlation existed between the stabilities of the adducts formed (as determined by other means) and the "internal shift" of the ethyl group in the ligand.* Although in all five of the cases studied (Et_3N, $EtMe_2N$, Et_2S, Et_2O, and EtMeO) no such correlation was found, the idea, that a correlation might exist between donor-acceptor properties and proton chemical shift, encouraged other research groups to examine other systems.

Holmes and Carter[35] examined the reaction of a series of dimethylamino-methylphosphines with triethylborane. The relative base strengths were determined by a displacement study, and the proton nmr data were examined for correlations. It was found that the change in chemical shift of the boron-attached ethyl

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* The term "internal shift" refers to the separation of the absorptions due to the methylene and methyl protons of an ethyl group, and is taken as positive when the methyl absorption is at higher field.

group* correlated well with adduct stability:

order of base strength as determined by displacement reactions		$\Delta\delta_{B-Et}$(ppm)*
(strongest)	$(CH_3)_3P$	+ 0.35 (farthest upfield)
	$> (CH_3)_3N$	+ 0.31
	$\approx (CH_3)_2PN(CH_3)_2$	+ 0.29
	$> (CH_3)_3P[N(CH_3)_2]_2$	+ 0.21
(weakest)	$> P[N(CH_3)_2]_3$	+ 0.11 (least downfield)

This correlation is explained in that coordination of $B(Et)_3$ to a basic center should increase the electron density on the ethyl groups attached to boron, causing an upfield shift of δ_{B-Et}, and that the more basic the ligand attached to the borane is, the greater that upfield shift should be.

Miller and Onyszchuk[36] reported the ^1H nmr shifts of the $(CH_3)_3N$ adducts of boron trihalides and borane and showed that the chemical shifts correlated with the previously determined[8] order of acceptor power: $BBr_3 > BCl_3 > BF_3 > 1/2(B_2H_6)$. In a related study, Miller and Onyszchuk reported[37] the ^1H nmr shifts of the CH_3CN adducts of boron trihalides and showed that these chemical shifts also correlated with the order of acceptor power.[2,3] All these values are shown below:

X in BX_3	δ of $(CH_3)_3N$ adduct†	δ of CH_3CN adduct**
H	159.5	

* δ_{B-Et} is determined by the moment method[39] referenced to cyclohexane. $\Delta\delta_{B-Et} = \delta_{adduct} - \delta_{free\ acid}$. A positive value indicates an upfield shift.

† Values in Hz, downfield from internal TMS, in $CHCl_3$ solution.

** Values in Hz, downfield from internal TMS, in CH_3NO_2 solution.

X in BX_3	δ of $(CH_3)_3N$ adduct	δ of CH_3CN adduct
F	157.3	161.8
Cl	180.2	182.8
Br	190.8	189.9
I	201.6[37]	

The idea in this correlation is that coordinating an acid to a base causes a net removal of electron density from the donor, thus deshielding protons in alkyl groups in the donor moiety. The greater the acceptor power of the acid, the greater should be the downfield shift of the alkyl protons in the donor group.

Other ^1H nmr data on donor-acceptor complexes are given in papers by Heitsch,[28] Hartman and Miller,[38] and Derek, Clague, and Danti.[40] Other papers which discuss donor-acceptor properties in terms of ^1H nmr shifts include those by Young, McAchran, and Shore,[41] Massey and Park,[42] Cowley and Mills,[43] and Clippard and Taylor.[44]

The correlation of relative acid strength of boron acids with changes in the ^1H nmr shift of protons in alkyl groups in the donor portion of donor-acceptor complexes formed between the acids and a reference hase is perhaps a difficult idea to accept. The basis of the argument is that the effect (a downfield shift when stronger acids are coordinated) is a deshielding due to the inductive withdrawing power of the acid. This argument clearly applies in those cases where there are only simple σ-bonding interactions between donor and acceptor. However, the effect of coordinating BX_3 groups (X = F, Cl, Br, I) is <u>opposite</u> to that expected on the hasis of the trend in electronegativity of the halogen suhstituents (that is, the most deshielding occurs when X = I, and the least when X = F). As

stated earlier, the effect has been attributed to the fact that the acid strength increases in the order:

$$BF_3 < BCl_3 < BBr_3 < BI_3,$$

and thus that the inductive withdrawal effect of the BX_3 group on coordinated donor groups should be in the same order. To evaluate this argument let us consider in detail the reason that the order of acid strength is $BF_3 < BCl_3 < BBr_3 < BI_3$. One can distinguish three major factors:

1) The order of electronegativity of the halogens is $F \gg Cl > Br > I$. On the basis of electronegativity alone, one would thus predict an order of $BF_3 \gg BCl_3 > BBr_3 > BI_3$. This order is opposite to the order observed.

2) The ability of the halogens to π-bond to boron (in the free acid) increases in the order $I < Br < Cl \ll F$. If π-bonding in the free acid must be destroyed to form the adduct, the strongest acid would be the one which has the least π-bonding. Thus, on the basis of extent of π-bonding, one would predict an order of $BF_3 \ll BCl_3 < BBr_3 < BI_3$. This order is the same as the order observed.

3) The relative steric bulk of the halogens increases in the order $F < Cl < Br < I$. Front strain in the adduct is a destabilizing influence, and one would predict that the acid strength, if determined by steric bulk alone, would be in the order $BF_3 > BCl_3 > BBr_3 > BI_3$. This order is opposite to the order observed.

If the actual order of acid strength is determined by these three factors, one must conclude that the predominant effect is that of factor 2), since only factor 2)

correctly predicts the order of acid strength. That is, the energy required to break up π-bonding in the free acid determines the trend in the relative acid strength of the boron trihalides.

It should be obvious then that if all of the π-bonding in the borane is destroyed in forming the adduct, the inductive withdrawing power of the coordinated borane would be determined by the other two factors, principally by the electronegativity of the halogens. Thus, the inductive withdrawing power should be in the order:

$$BF_3 > BCl_3 > BBr_3 > BI_3$$

To the extent that there is residual π-bonding or "memory of the free acid" in the acceptor portion of the adduct, this order may be modified somewhat, but it is difficult to believe that there could be enough residual π-bonding in the adduct to cause the order of inductive withdrawal power of the coordinated borane to be the reverse of that predicted by electronegativity considerations.* One must conclude therefore that some other factors besides inductive effect are at work in determining the chemical shifts of these adducts. It is the purpose of this

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* It must be pointed out that this argument is not without conflicting evidence. Arguments in favor of residual π-bonding in these donor-acceptor molecules have become common in the recent literature, and certainly experimental evidence exists supporting the idea of such residual π-bonding being a factor in these systems. The argument for residual π-bonding is best put forward by Brown, Drago, and Bolles;[17] additional experimental evidence is presented by Swanson, Shriver, and Ibers,[10] Clippard, Hanson, and Taylor,[12] and Lanthier and Miller.[16] Nevertheless, even if residual π-bonding does play a role in the bonding of these adducts, one should expect the opposing effects to cancel out in all the haloboranes except perhaps BF_3. The fact that large changes in chemical shift occur between BCl_3 and BBr_3 and especially between BBr_3 and BI_3 coordinated to a reference base would seem to clearly indicate that the explanation of the trend in chemical shifts in terms of inductive withdrawal effects is at least incomplete, if not altogether wrong.

work to present evidence which supports one such factor — steric interaction between the halogens on boron and protons on alkyl groups in bases coordinated to boron.

CHAPTER II

MATERIALS AND PROCEDURES

Materials

Trimethylamine-borane, dimethylamine-borane, and triethylamine-borane were obtained from Callery Chemical Company and were used without further purification. Other chemicals and solvents were reagent grade and, except where noted, were used without further purification, but were dried over Molecular Sieve 3A where appropriate.

Apparatus and Methods

Infrared spectra were obtained using a Beckman IR-10 spectrophotometer. Solid samples were prepared as KBr pellets; liquid samples were prepared as liquid films between KBr plates.

Melting points were recorded on a Thomas-Hoover apparatus and were not corrected.

Elemental analyses were performed by Peninsular Chem-Research, Inc., Gainesville, Florida.

Except where noted, proton nmr spectra of the amine-boranes and haloboranes were recorded at ambient temperatures in CH_2Cl_2 solution with tetramethylsilane as an internal standard. Concentrations were typically in the range 0.25 to 0.65 M, although some of the diethylamine-haloborane spectra were obtained on more concentrated solutions. The spectra were obtained at 60 MHz, using a Varian Model A60-A spectrometer. The chemical shifts are reported in Hz, downfield from internal tetramethylsilane. In two cases, to be mentioned later, spectra

were also obtained at 100 MHz, using a Varian Model XL-100 spectrometer. Calibration of the spectra of the diethylamine-haloboranes was accomplished by means of sidebands generated from the peak due to internal tetramethylsilane.

Computer Analysis of ^{1}H NMR Spectra of Diethylamine-Haloboranes

The ^{1}H nmr spectra of the diethylamine-haloborane adducts were analyzed by means of the program LAMP2, a version of LAME,[45] written for an IBM 360-65 computer with a Calcomp plotter, and kindly supplied by Dr. R.W. King of the University of Florida Chemistry Department. LAME is a modification of LAOCOON3[46,47] to include magnetic equivalence factoring, which allows a group of magnetically equivalent nuclei to be treated as one nucleus of spin equal to the total spin of the group, as regards interaction with other nuclei, but which weights the energy level populations for the group according to the binominal expansion. This modification greatly simplifies the calculation in cases where such groups of magnetically equivalent nuclei exist.

The program LAMP2 is made up of three different subroutines: non-iterative, iterative, and plot.

The non-iterative subroutine has the capability of causing the computer to generate, from an arbitrarily chosen set of chemical shifts and coupling constants for a system of two to seven groups of magnetically equivalent nuclei of spin-1/2, a table of frequencies and intensities of the lines expected in the nmr spectrum. The program uses the input data to form and solve the Hamiltonian matrix for the stationary state energies of the system, following the procedures outlined by Pople, Schneider, and Bernstein.[48] The frequencies of allowed transitions correspond to energy differences of the stationary states giving rise to the transition.

If a spectrum thus calculated bears a recognizable resemblance to an observed spectrum, the iterative subroutine can cause the computer to perform an iterative calculation by means of which the calculated frequencies of assigned lines are brought as close as possible (by the least-squares criterion) to the corresponding observed lines. The chemical shifts and coupling constants which yield this best fit are then printed out along with information about the expected error in them and along with a table of observed and calculated line frequencies, calculated intensities, and errors in fitting the frequencies of observed lines.

The procedure involved in the iterative subroutine is as follows. The partial derivatives $\delta\nu_i/\delta p_j$ are found in the region of the input parameters, where $\delta\nu_i/\delta p_j$ is the rate of change of the i-th line position with respect to the j-th parameter. For small, finite changes, one assumes that $\Delta\nu_i = (\delta\nu_i/\delta p_j)\Delta p_j$. During each cycle of the iteration the program seeks to correct each parameter by the amount required to produce agreement with experiment. This produces equations of the form, $\sum_j (\delta\nu_i/\delta p_j)\Delta p_i = (\nu_{obs} - \nu_{calc})_i$, for each selected line position ν_i. In matrix form this group of equations becomes $\underline{D}\Delta = N$, where $\underline{D}$ is the (ixj) matrix of partial derivatives, Δ is a row matrix of corrections to the j parameters, and N is the column matrix of i line position errors. As long as $i > j$, the equations are overdetermined, and if the initial guesses are good, the program is strongly convergent. A best least-squares fit to observed line positions is sought, rather than exact agreement.

It should be emphasized that iterative programs typically seek convergence either on energy levels or on transition frequencies (i.e. , differences between

energy levels). The program used in this work iterates to convergence on transition frequencies.

The plot subroutine can cause the computer, using the Calcomp plotter, to generate a calculated spectrum, based on Castellano's hybrid line shape function,[49] which includes a histogram showing exact line positions.

The spectra of these diethylamine-haloborane adducts were analyzed as an $ABCD_3$ spin system (A, B = non-equivalent methylene protons; C = nitrogen proton; D_3 = methyl protons) since the full eleven-proton system was too large for the program as currently dimensioned. Little error should be introduced by this approximation, since any cross-coupling between the ethyl groups should be exceedingly small, and since the nitrogen-attached proton is only weakly coupled to all others ($J/\Delta\delta$ does not exceed 0.1). The system approximates to $ABMX_3$.

The 100 MHz spectra of the dibromo- and monochloroborane adducts of diethylamine were obtained, and analysis of these, made simpler by the spreading out of the pattern at the higher field strength, allowed subsequent assignments in the 60 MHz spectra to be made with more certainty. The initial assignment of parameters was made as follows. Values of δ for the various protons were estimated by visual approximation. The centers of mass of the two halves of the methylene pattern were used as initial estimates of δ_{CH_2}(A) and δ_{CH_2}(B). The two $J_{CH_2-CH_3}$'s were assumed to be approximately equal, since, in every case, the methyl resonances were 1:2:1 triplets; the value used was the spacing of the triplet. Values for J_{NH-CH_2} were assumed to be either zero, by visual observation, or about 5Hz, by analogy to the dimethylamine-haloborane results.

Values for J_{AB} were estimated visually on the basis of spacings in the methylene pattern. Signs for the coupling constants were assumed to be positive for the 3-bond constants ($J_{CH_2-CH_3}$ and J_{NH-CH_2}) and negative for the 2-bond constant (J_{AB}) by analogy to carbon systems. After one spectrum had been fully analyzed, assignment of parameters in other spectra were made by a straightforward comparison of patterns and/or by visual estimations.

The spectra of diethylamine-trichloro- and tribromoborane were poorly resolved, probably due to the added feature of coupling to boron, and as a result it was not possible to carry out full analyses on these two spectra. Approximate values for the parameters were obtained by simulating the spectra. The accuracy of these results is obviously somewhat lower than those for the six mono- and dihaloborane adducts, which results were obtained by rigorous analysis.

No fine structure was observed in any of the NH resonances, probably on account of quadrupolar broadening by coupling to nitrogen and/or boron. Accordingly, approximate chemical shifts were assigned to these resonances, and these shifts were not refined.

On the average, 20 of 48 lines (and in no case less than 17) were assigned in the methylene region of a spectrum and were given equal weight. In each case 16 of 32 lines were assigned in the methyl region. The root-mean-square error of observed vs. calculated transition frequencies did not exceed 0.25 Hz and averaged 0.16 Hz. Good agreement was found between observed 60 MHz spectra and calculated spectra as plotted by the computer. These observed and calculated spectra are shown in the experimental section.

CHAPTER III

SYNTHESES AND REACTIONS

The syntheses of amine-haloborane adducts examined in this study were accomplished by following methods established in previous work in this laboratory, which involved the preparation of mono-, di-, and trihaloborane adducts of trimethylamine and pyridine via halogenation of the respective amine-borane.[24,25,50-52] In that work it was determined that pyridine-borane was more reactive than trimethylamine-borane towards various halogenating agents. The reactions of interest to the work discussed here are shown in the equations which follow ($TMA = (CH_3)_3N$, $py = C_5H_5N$):

(1) $TMABH_3 + HX \rightarrow TMABH_2X + H_2$ (X = Cl, Br)*

(2) $TMABH_3 + 1/2X_2 \rightarrow TMABH_2X + 1/2H_2$ (X = I)

(3) $TMABH_3 + 3/2X_2 \rightarrow TMABHX_2 + 1/2H_2 + HX$ (X = Br, I)†

(4) $TMABH_3 + 5/2X_2 \rightarrow TMABX_3 + 1/2H_2 + 2HX$ (X = Cl, Br, I)**

(5) $TMA + BX_3 \rightarrow TMABX_3$ (X = F, Cl, Br, I)

(6) $pyBH_3 + HX \rightarrow pyBH_2X + H_2$ (X = Cl, Br)

(7) $pyBH_3 + 1/2X_2 \rightarrow pyBH_2X + 1/2H_2$ (X = I)

(8) $pyBH_3 + 2HX \rightarrow pyBHX_2 + 2H_2$ (X = Cl, Br)‡

(9) $pyBH_3 + X_2 \rightarrow pyBHX_2 + H_2$ (X = I)

(10) $pyBH_3 + 2X_2 \rightarrow pyBX_3 + H_2 + HX$ (X = Cl, Br)††

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* This reaction proceeds no farther, even with excess HX, unless the solution is heated to about 100°.

† Reflux is required for X=I. Reaction produces a mixture of products for X=Cl.

** Reaction stoichiometry is assumed for X=Cl. Reflux is required for X=I.

‡ The reaction proceeds no farther, even with excess HX and heating.

†† Reaction stoichiometry is assumed for X=Cl.

In some preliminary experiments, it was established that triethylamine-borane reacted in a fashion similar to trimethylamine-borane, and that dimethyl- and diethylamine-borane reacted in a fashion similar to pyridine-borane. If, as has been suggested in some of the work previously cited,[25, 52] these reactions are affceted by steric requirements in the reacting molecule, it is reasonable that tertiary amine-boranes should all react similarly and that secondary amine-boranes should reaet more easily, hence the resemblance to pyridine-borane which also presents less steric bulk.

Preparation of Triethylamine-Haloboranes

Reaction of triethylamine-borane and chlorine. -- The reaction of triethylamine-borane and chlorine was examined by monitoring the change in the nmr spectrum of a solution of $(CH_3CH_2)_3NBH_3$ in CH_2Cl_2 as a function of the amount of Cl_2 added. The original pattern for $(CH_3CH_2)_3NBH_3$ (a triplet in the methyl region and a quartet in the methylene region) was observed to diminish in intensity as a new triplet and quartet grew downfield from the original triplet and quartet. This new set of peaks grew to a maximum then began to diminish as a third set of peaks (again a triplet and a quartet) grew downfield from the second set. As this third set of peaks grew to a maximum and began to diminish, a fourth set of peaks (a triplet and a eomplex multiplet) emerged downfield from the third set. This fourth set grew to a maximum as the other three sets disappeared, and did not diminish on further addition of Cl_2. These observations are explained on the basis of stepwise chlorination of $(CH_3CH_2)_3NBH_3$, producing successively $(CH_3CH_2)_3NBH_2Cl$, $(CH_3CH_2)_3NBHCl_2$, and finally $(CH_3CH_2)_3NBCl_3$. The reaction was such as to produce a ternary

system at most points in the reaction; that is, before all the starting material had been monochlorinated, some of the product monochloroborane adduct had been dichlorinated to give dichloroborane adduct. The nmr spectrum observed for $(CH_3CH_2)_3NBCl_3$ is the same as that reported by Miller and Onyszchuk,[36] who prepared $(CH_3CH_2)_3NBCl_3$ by direct combination of $(CH_3CH_2)_3N$ and BCl_3. The spectrum reported here gave better resolution of lines so that the tentative assignment of Miller and Onyszchuk is confirmed. The complex multiplet in the methylene region of the spectrum of $(CH_3CH_2)_3NBCl_3$ was produced by coupling of the CH_2 protons to boron as well as to the CH_3 protons. The pattern (Figure 1) actually appeared as a 13-peak multiplet because of overlap of some of the peaks in the expected 16-peak pattern.

The chemical shifts and coupling constants for these adducts are given in Table III.

Reaction of triethylamine-borane and bromine. -- The reaction of triethylamine-borane and bromine was also examined by monitoring the change in the nmr spectrum of a solution of $(CH_3CH_2)_3NBH_3$ in CH_2Cl_2 as a function of the amount of Br_2 added. As in the reaction of $(CH_3CH_2)_3NBH_3$ and Cl_2, the peaks due to starting material were replaced by two sets of peaks (each set consisting of a triplet and a quartet) downfield from the original set, which successively increased and then decreased in intensity as more bromine was added. These two sets of triplets and quartets were due to $(CH_3CH_2)_3NBH_2Br$ and $(CH_3CH_2)_3NBHBr_2$ respectively. A triplet and a complex multiplet appeared downfield of the triplet and quartet of $(CH_3CH_2)_3NBHBr_2$ as more Br_2 was added, and this set of peaks grew to a maximum and did not diminish on further addition

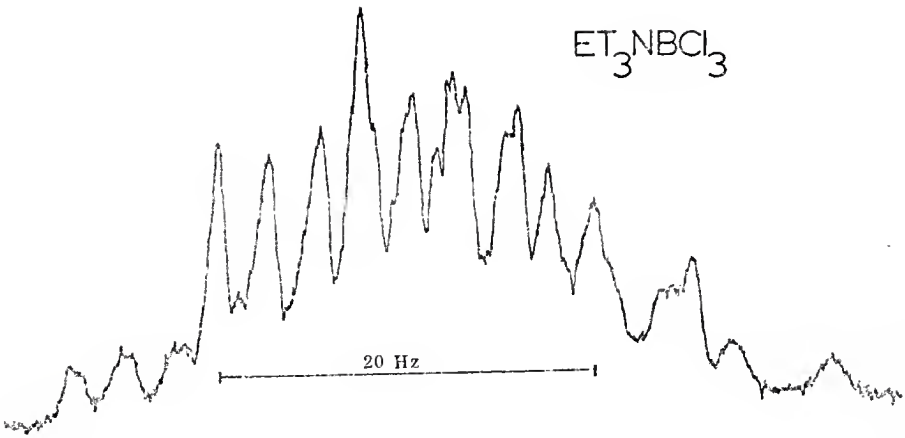

Figure 1. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_3NBCl_3$.

of Br_2. This fourth set of peaks was due to $(CH_3CH_2)_3NBBr_3$. The multiplet in the CH_2 region (Figure 2) showed 15 peaks of the expected 16-peak pattern, one peak being masked by a ^{13}C satellite of the solvent, CH_2Cl_2.

The chemical shifts and coupling constants for these adducts are given in Table III.

The ^{11}B nmr spectrum of $(CH_3CH_2)_3NBHBr_2$ showed a doublet (J_{BH} = 161 Hz) centered at 20.3 ppm upfield from trimethylborate.

Reaction of triethylamine-borane and iodine. -- The reaction of triethylamine-borane and iodine was likewise examined by monitoring the change in the nmr spectrum of a solution of $(CH_3CH_2)_3NBH_3$ in CH_2Cl_2 as a function of the amount of I_2 added. Triethylamine-borane (2.22 g, 19.3 mmol) was dissolved in 25 ml of CH_2Cl_2. Solid iodine (2.44 g, 9.62 mmol) was added in portions with stirring. The nmr spectrum of this solution showed a triplet in the methyl region and a quartet in the methylene region, each downfield from the triplet and quartet of the starting material. This pattern is due, therefore, to $(CH_3CH_2)_3N$-BH_2I.

To the solution of $(CH_3CH_2)_3NBH_2I$ in CH_2Cl_2 prepared above, more iodine (3.21 g, 12.6 mmol) was added with stirring and reflux. The nmr spectrum of this solution, taken several times over a period of about 20 hours, showed the triplet and quartet due to $(CH_3CH_2)_3NBH_2I$ slowly disappearing, while a new triplet and quartet appeared downfield. After 22 hours of reflux, the new triplet and quartet were the only peaks in the spectrum other than solvent peaks. These peaks thus correspond to $(CH_3CH_2)_3NBHI_2$.

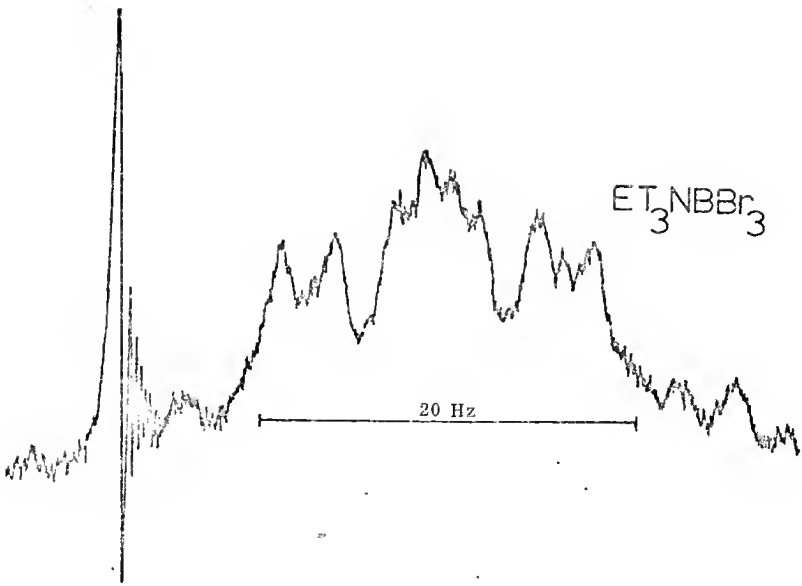

Figure 2. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_3NBBr_3$.

The ^{11}B nmr spectrum of $(CH_3CH_2)_3NBHI_2$ showed a doublet (J_{BH} = 155 Hz) centered at 42.5 ppm upfield from trimethylborate.

To the solution of $(CH_3CH_2)_3NBHI_2$ in CH_2Cl_2 prepared above, more iodine (4.89 g, 19.3 mmol) was added with stirring and reflux. The nmr spectrum of this solution still showed only the triplet and quartet due to $(CH_3CH_2)_3NBHI_2$ after a short (1/2 hour) period of reflux, but the spectrum taken after about 4 hours of reflux showed a new set of peaks, the peaks for $(CH_3CH_2)_3NBHI_2$ having almost disappeared. This new set of peaks was a triplet in the methyl region and a doublet of quartets in the methylene region. On refluxing for an additional 24 hours, the new pattern remained unchanged. This pattern is not consistent with $(CH_3CH_2)_3NBI_3$, but is consistent with $(CH_3CH_2)_3NH^+$.

Accordingly, a sample of $(CH_3CH_2)_3NH^+I^-$ was prepared and its nmr spectrum in CH_2Cl_2 obtained. To this solution, some iodine was added, so as to give $(CH_3CH_2)_3NH^+I_3^-$, and the nmr spectrum again obtained. Both spectra were very similar in pattern and position to the spectrum obtained above, namely, a doublet of quartets in the methylene region and a triplet in the methyl region. As a final check, the two solutions [$(CH_3CH_2)_3NH^+I_3^-$ and the unknown solution above] were mixed and the nmr spectrum taken. The spectrum showed only one set of peaks, the pattern being unchanged from the spectra of the solutions taken separately. Therefore, the product of the exhaustive iodination of $(CH_3CH_2)_3NBH_3$ is not $(CH_3CH_2)_3NBI_3$, but is instead $(CH_3CH_2)_3NH^+A^-$, where $A^- = I_3^-$ (or some other anion).

The chemical shifts and coupling constants for these adducts are given in Table III.

Reaction of triethylamine and boron trifluoride-etherate. -- A solution of triethylamine in ether was added dropwise to an ether solution of boron trifluoride-etherate. Evaporation of the volatiles left low-melting, colorless crystals of triethylamine-trifluoroborane. On standing in air these crystals slowly decomposed to a brown oil. An nmr spectrum of this material in CH_2Cl_2 solution showed a triplet in the methyl region and a broadened quartet in the methylene region. The chemical shifts and coupling constants are given in Table III.

Preparation of Dimethylamine-Haloboranes

Synthesis of dimethylamine-mono- and dichloroborane. -- $(CH_3)_2NHBH_2Cl$ and $(CH_3)_2NHBHCl_2$ were prepared by V.R. Miller[53] by the reaction of HCl and $(CH_3)_2NHBH_3$. These procedures were confirmed in this present work, and the nmr data for these two compounds, quoted from Miller's work, are given in Table II.

Synthesis of dimethylamine-trichloroborane.[54] -- $(CH_3)_2NHBH_3$ (1.90 g, 32.2 mmol) was dissolved in 25 ml of CH_2Cl_2. Gaseous Cl_2 was bubbled into this solution at a moderate rate, with stirring, until the solution turned yellow. At this time a white solid was present, and the flask was warm from the reaction. All the volatiles were stripped off by pumping on a rotary evaporator, leaving a light yellow solid. The product was stirred with 25 ml of fresh CH_2Cl_2 and then 20 ml petroleum ether was added to precipitate the portion of the product that was in solution. The white solid thus obtained was filtered, washed with two 5 ml portions of petroleum ether, and dried by pumping. The yield was 4.56 g (28.1 mmol; 87.0%, based on $(CH_3)_2NHBH_3$), mp = 125-7°. Anal. Calcd. for $C_2H_7NBCl_3$: C, 14.81; H, 4.35; N, 8.63. Found: C, 14.87; H, 4.52; N, 8.27.

The infrared spectrum of $(CH_3)_2NHBCl_3$ (Figure 3) is characterized by a sharp band at 3180 cm^{-1}, assigned to N-H stretch, and a broad band at 700-780 cm^{-1}, assigned to coordinated BCl_3 vibrations.[55] The sharp band at 900 cm^{-1}, which Gerrard[56] assigned to BCl_2^+, is probably due to C-N stretch.[55] The entire infrared spectrum is given in Table I.

The proton nmr spectrum (Figure 4) showed a 1:1:2:2:1:1 sextet in the aliphatic region. This pattern arises from coupling of the methyl protons with both the nitrogen-attached proton and boron, giving a doublet of quartets; the coupling constants are such as to cause overlapping of two sets of two peaks. The chemical shift and coupling constants are given in Table II.

The ^{11}B nmr spectrum showed a single peak at 9.4 ppm upfield from trimethylborate.

Reaction of dimethylamine-borane and bromine. -- Dimethylamine-borane (0.651 g, 11.0 mmol) was dissolved in 30 ml of CH_2Cl_2. Bromine (0.885 g, 5.54 mmol), dissolved in 5 ml of CH_2Cl_2, was added dropwise with stirring. The nmr spectrum of this solution consisted of a strong doublet downfield from the doublet due to starting material. There was a small amount of starting material left, since the doublet due to starting material had not entirely disappeared. There was also evidence for a third product since a small peak was observed downfield from the strong doublet. These observations are consistent with most of the $(CH_3)_2NHBH_3$ having been converted to $(CH_3)_2NHBH_2Br$, plus a little $(CH_3)_2NHBHBr_2$.

To the solution of $(CH_3)_2NHBH_2Br$ in CH_2Cl_2 prepared above, more bromine (0.914 g, 5.72 mmol), dissolved in 5 ml of CH_2Cl_2, was added slowly with stirring.

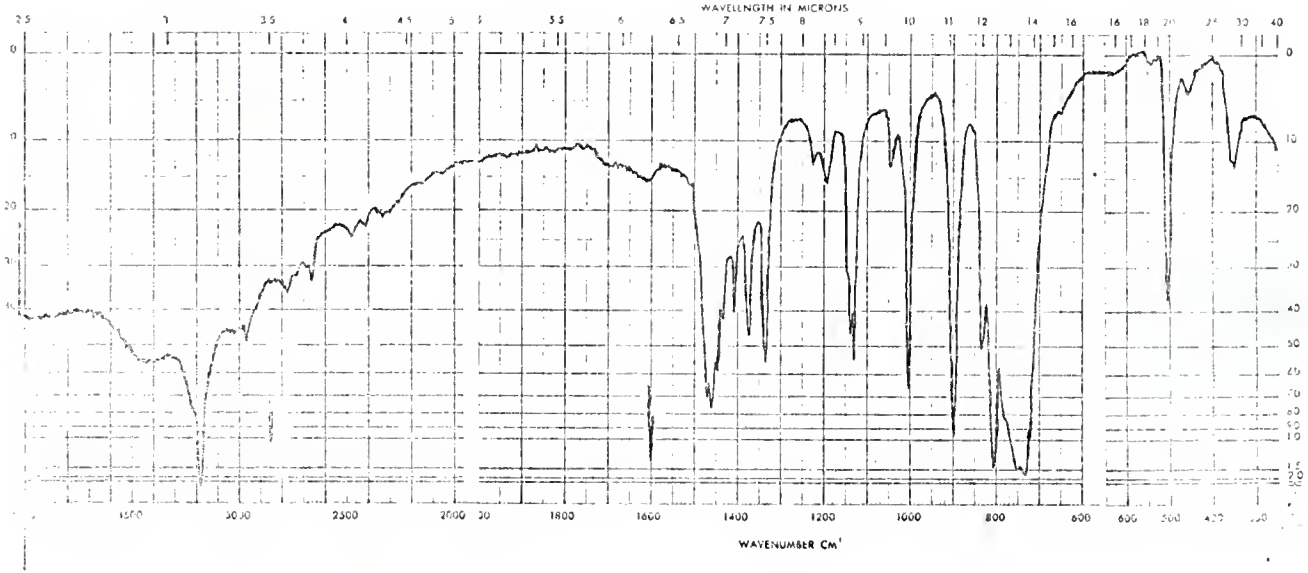

Figure 3. Infrared spectrum of $(CH_3)_2NHBCl_3$.

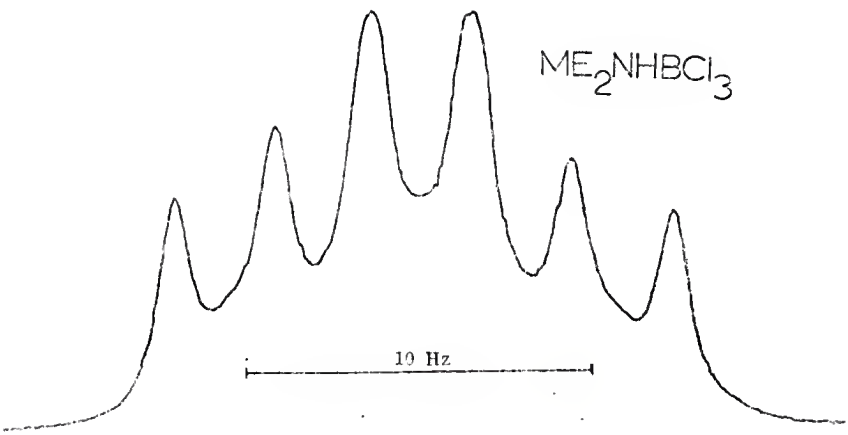

Figure 4. ^{1}H nmr spectrum of $(CH_3)_2NHBCl_3$.

The nmr spectrum of this solution showed the doublet assigned to $(CH_3)_2NHBH_2Br$ to have nearly disappeared and the doublet assigned to $(CH_3)_2NHBHBr_2$ to have become very strong. There was a shoulder on the downfield side of the $(CH_3)_2NHBHBr_2$ doublet which was assigned to a small amount of $(CH_3)_2NHBBr_3$.

To the solution of $(CH_3)_2NHBHBr_2$ in CH_2Cl_2 prepared above, more bromine (0.986 g, 6.17 mmol), dissolved in CH_2Cl_2, was added slowly with stirring. The nmr spectrum of this solution showed the doublet previously assigned to $(CH_3)_2NHBHBr_2$, reduced somewhat in intensity, along with a complex pattern of similar intensity at the position of the shoulder previously assigned to $(CH_3)_2NHBBr_3$. More bromine was added to this solution until a permanent color was produced. The nmr spectrum of this solution showed only the complex pattern assigned to $(CH_3)_2NHBBr_3$. Chemical shifts and coupling constants for these adducts are given in Table II.

Synthesis of dimethylamine-tribromoborane.[54] -- $(CH_3)_2NHBH_3$ (2.95 g, 50.0 mmol) was dissolved in 40 ml of dry CH_2Cl_2. Br_2 (16.05 g, 100.4 mmol) was dissolved in 40 ml of dry CH_2Cl_2. The Br_2 solution was added dropwise, with vigorous stirring, to the $(CH_3)_2NBH_3$ solution. As the last of the Br_2 solution was added, a white precipitate formed, and the solution, which was previously colorless, turned slightly yellow. All the volatiles were stripped off by pumping on a rotary evaporator. The white solid which remained was taken, still in the flask, into a drybox where the product was transferred to a tared bottle. The yield was 13.0 g (44.0 mmol; 88.0%, based on $(CH_3)_2NHBH_3$), mp = 150.5-152°. Anal. Calcd. for $C_2H_7NBBr_3$: C, 8.13; H, 2.39; N, 4.74; Br, 81.09. Found: C, 8.14; H, 2.36; N, 4.64; Br, 81.21.

The infrared spectrum of $(CH_3)_2NHBBr_3$ (Figure 5) showed a strong, sharp band at 3150 cm^{-1}, assigned to N-H stretch, and a broad band at 650-700 cm^{-1}, assigned to coordinated BBr_3 vibrations.[55] The entire infrared spectrum is given in Table I.

The proton nmr spectrum (Figure 6) showed a multiplet in the aliphatic region, which resembles a sextet of 1:1:2:2:1:1 intensity, but which shows eight peaks under high resolution. The pattern is a doublet of quartets due to coupling of the methyl protons with both the nitrogen-attached proton and boron. The chemical shift and coupling constants are given in Table II.

The ^{11}B nmr spectrum showed a single peak at 24.8 ppm upfield from trimethylborate.

Reaction of dimethylamine-borane and iodine. -- To dimethylamine-borane (0.534 g, 9.06 mmol), dissolved in 20 ml of CH_2Cl_2, was added solid iodine (1.14 g, 4.49 mmol) piecewise with stirring. The nmr spectrum of the resulting solution showed only a doublet downfield from the position of the doublet due to starting material. This doublet was thus assigned to $(CH_3)_2NHBH_2I$.

The ^{11}B nmr spectrum of $(CH_3)_2NHBH_2I$ showed a triplet (J_{BH} = 143 Hz) centered at 31.0 ppm upfield from trimethylborate.

To dimethylamine-borane (1.05 g, 17.8 mmol) in 25 ml CH_2Cl_2 was added iodine (4.52 g, 17.8 mmol), piecewise with stirring. The nmr spectrum of the resulting solution, taken 45 minutes after all the I_2 had been added, showed a strong doublet downfield from the position of the doublet previously assigned to $(CH_3)_2NHBH_2I$. This doublet was assigned to $(CH_3)_2NHBH_2$. There was in the spectrum a small peak corresponding to the right-hand peak of the doublet due to

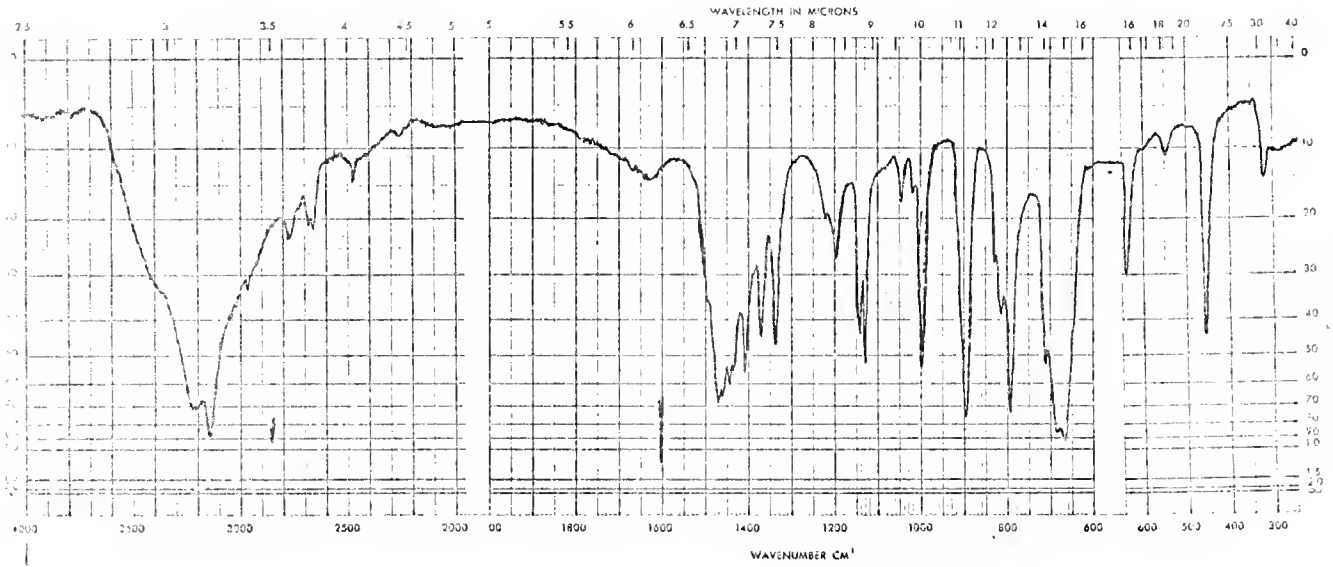

Figure 5. Infrared spectrum of $(CH_3)_2NHBBr_3$.

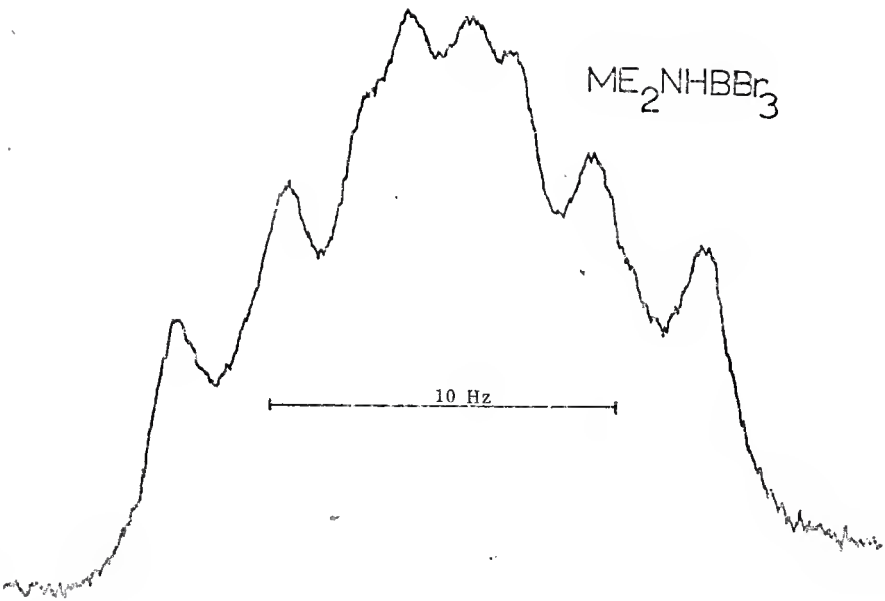

Figure 6. ^{1}H nmr spectrum of $(CH_3)_2NHBBr_3$.

$(CH_3)_2NHBH_2I$. The left-hand peak would be masked by the doublet assigned to $(CH_3)_2NHBHI_2$. The spectrum taken after 5 hours showed only the doublet assigned to $(CH_3)_2NHBHI_2$.

The chemical shifts and coupling constants for these adducts are given in Table II.

The ^{11}B nmr spectrum of $(CH_3)_2NHBHI_2$ showed a doublet (J_{BH} = 158 Hz) centered at 43.5 ppm upfield from trimethylborate.

Synthesis of dimetbylamine-triiodoborane. -- $(CH_3)_2NHBH_3$ (2.5 g, 42 mmol) was dissolved in 40 ml of dry CH_2Cl_2 and I_2 was added piece by piece with stirring until a permanent color was given to the solution (about 21 mmol of I_2 was required). A large excess of I_2 was then added (at least 100 mmol), and the solution was refluxed for about 40 hours. After refluxing, the volatiles were removed on a rotary evaporator. A black, fuming solid remained in the flask. Fresh CH_2Cl_2 (40 ml) was added to this solid. To this solution about 3 ml of mercury was added, and the mixture was vigorously stirred for 15 minutes. At this time the solution was decolorized, and solid HgI_2 was observed in the flask. The contents of the flask were filtered.* Hexane was added to tbe filtrate, producing a light tan precipitate. This solid was filtered off, washed with two 5 ml portions of hexane, and pumped dry. Tbe yield was 6.0 g (14 mmol; 33%, based on $(CH_3)_2NHBH_3$), mp = 157-158° (some evidence of decomposition at 83-85°). Anal. Calcd. for $C_2H_7NBI_3$: C, 5.50; H, 1.62; N, 3.21. Found: C, 5.62; H, 1.64; N, 3.04.

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* Dimethylamine-trihaloboranes have a low solubility in CH_2Cl_2; therefore, this is a yield-reducing step.

The infrared spectrum of $(CH_3)_2NHBI_3$ (Figure 7) is characterized by a broad band at 3300-2950 cm^{-1} (with peaks at 3210 and 3110 cm^{-1}) due to N-H stretch, and a doublet at 615 and 600 cm^{-1}, probably due to B-I stretch.[55] The entire infrared spectrum is given in Table I.

The proton nmr spectrum (Figure 8) showed a multiplet in the aliphatic region, which resembles a quintet of 1:2:2:2:1 intensity, but which shows eight peaks under higb resolution. The pattern is a doublet of quartets due to coupling of tbe methyl protons with both the nitrogen-attached proton and boron. Tbe chemical shift and coupling constants are given in Table II.

Synthesis of dimethylamine-trifluoroborane. -- [This is tbe only dimethylamine-trihaloborane which can be prepared pure by direct addition of amine and borane. Two different methods exist for the preparation of dimethylamine-trifluoroborane. The adduct may be prepared by direct addition of dimethylamine to boron trifluoride[57] (in tbe gas phase or in an inert solvent), or the adduct may be prepared via a displacement reaction, typically the reaction of dimethylamine with boron trifluoride-etherate.[58]]

Both metbods were used in this study, and the best results were obtained when the two gases were bubbled together in an inert solvent (CH_2Cl_2). Care should be taken to keep BF_3 in slight excess. The product of this reaction, isolated by pumping off the volatiles on a rotary evaporator, was a white crystalline solid, mp = 40-44°. Anal. Calcd. for $C_2H_7NBF_3$: C, 21.28; H, 6.25; N, 12.41. Found: C, 20.90; H, 5.70; N, 12.16.

The infrared spectrum of $(CH_3)_2NHBF_3$ (Figure 9) was broad and poorly resolved, probably because of the low melting point of the crystals. It is

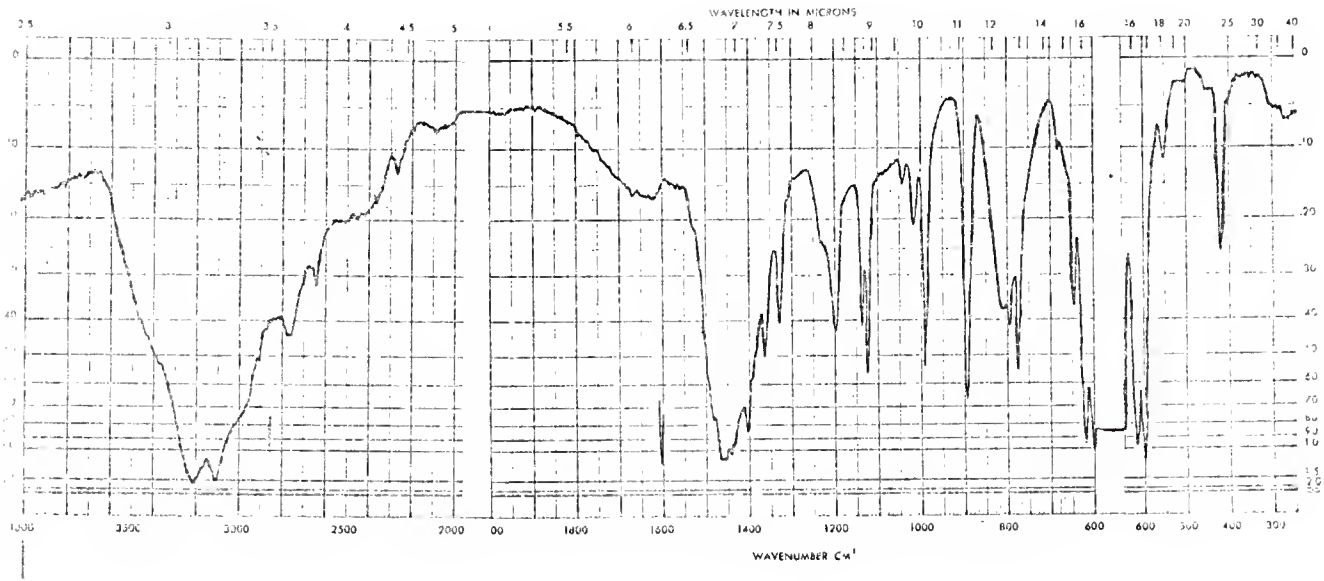

Figure 7. Infrared spectrum of $(CH_3)_2NHBI_3$.

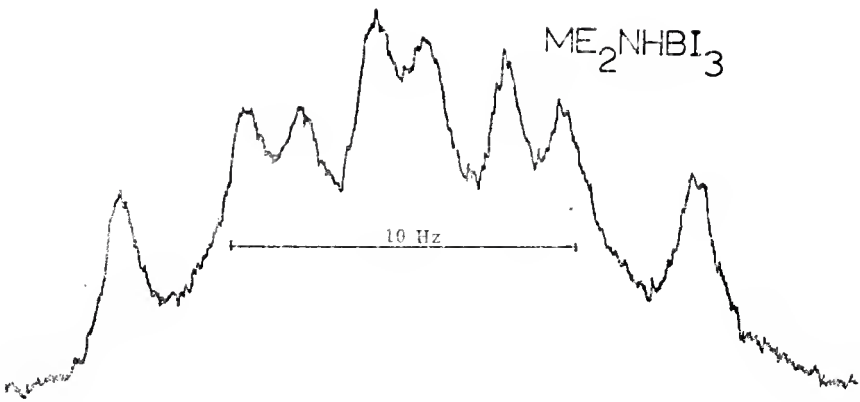

Figure 8. ^{1}H nmr spectrum of $(CH_3)_2NHBI_3$.

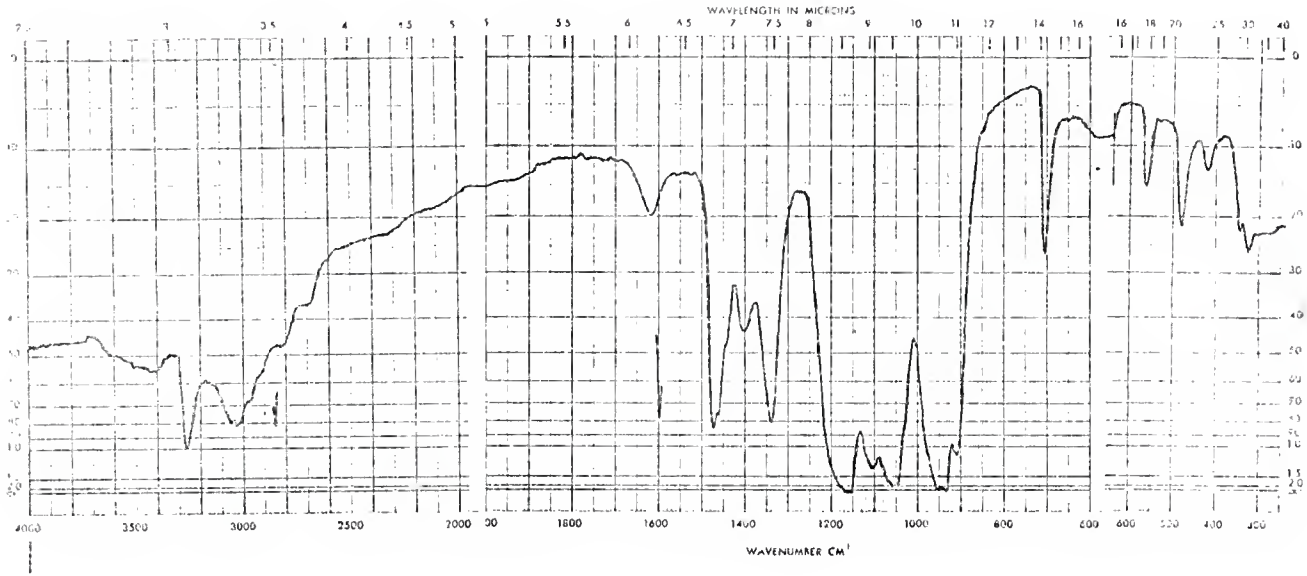

Figure 9. Infrared spectrum of $(CH_3)_2NHBF_3$.

characterized by a band at 3260 cm^{-1}, assigned to N-H stretch, and a set of three broad, ill-defined bands at 1210-1150, 1120-1040, and 980-900 cm^{-1}, probably due respectively to B-F stretch, CH_3 wag, and a combination of B-F stretch and C-N stretch.[55] The sharp peak at 705 cm^{-1} is probably due to B-N stretch.[40] The entire infrared spectrum is given in Table I.

The proton nmr spectrum (Figure 10) showed a 1:1:1:2:1:1:1 septet in the aliphatic region. This pattern arises from coupling of the methyl protons to both the nitrogen-attached proton and boron;[40] the coupling constants are such as to cause the overlapping of two of the expected 8 peaks. The chemical shift and coupling constants are given in Table II.

Reaction of Dimethylamine and Boron Trihalides

Reaction of dimethylamine and boron trichloride. -- Boron trichloride (1.50 ml, 18.3 mmol) was dissolved in 50 ml of dry benzene on a vacuum line (the pressure of the solution was 120 mm). Dimethylamine (1.20 ml, 18.3 mmol) was trapped out on another part of the line and allowed to warm up. When the pressure of dimethylamine reached 500 mm, the stopcock to the BCl_3-benzene solution was opened, allowing the dimethylamine to enter at such a rate as to hold the pressure of dimethylamine in the external system steady at 500 mm; a white solid precipitated during this procedure. The addition was facilitated by stirring. After all the dimethylamine had been transferred into the BCl_3-benzene solution, the volatiles were removed by evacuation, leaving a white solid in the flask. After transfer to a tared vial, the product weighed 2.55 g (86% yield).

A small amount (about 0.2 g) of this product was stirred with 20 ml of CH_2Cl_2 for three hours. The solution was filtered, giving a white solid (A). The

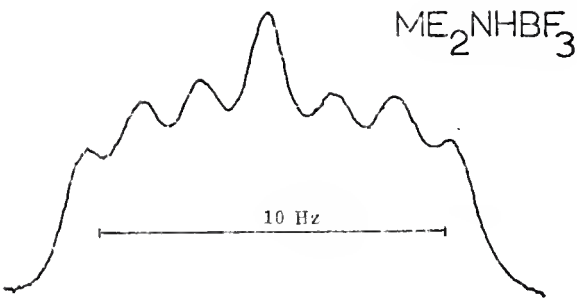

Figure 10. ^{1}H nmr spectrum of $(CH_3)_2NHBF_3$.

solvent was removed from the filtrate on a rotary evaporator, leaving a second white solid (B). Each fraction consisted of about 0.1 g of material.

An nmr spectrum was taken in CH_2Cl_2 solution of the CH_2Cl_2-soluble material (B), which showed a seven-peak multiplet in the aliphatic region. This multiplet was the result of an overlapping of two resonances: 1) a 1:1:2:2:1:1 sextet, centered at 172 Hz, due to the 1:1 adduct, $(CH_3)_2NHBCl_3$, and 2) a 1:2:1 triplet, centered at 167.5 Hz, due to dimethylammonium ion, $(CH_3)_2NH_2^+$ (J_{HNCH} = 5.7 Hz). The relative proportions of these two species was determined (by estimating visually) to be about 5:1, the adduct in excess. The infrared spectrum of this fraction (B) was similar to that of authentic $(CH_3)_2NHBCl_3$, but there were some small differences. A small peak was observed at 650 cm^{-1}, which was probably due to BCl_4^- ion.[59] A broad band at 3050-2920 cm^{-1}, two sharp peaks at 2680 and 2600 cm^{-1}, and two sharp peaks at 2680 and 2600 cm^{-1} were probably caused by $[(CH_3)_2NH]_2BCl_2^+$. The absence of strong peaks at 2440 and 1025 cm^{-1} indicates the absence of $(CH_3)_2NH_2^+$ in fraction (B). The ammonium ion observed in the nmr spectrum of fraction (B) must then have oome from the hydrolysis of $[(CH_3)_2NH]_2BCl_2^+$. Since unhydrolyzed $[(CH_3)_2NH]_2BCl_2^+$ ion would not have been distinguishable in the nmr (δ = 167 Hz in CH_2Cl_2, about 15 Hz broad), one cannot judge the relative proportions of adduct and boronium salt from the ratio of adduct to ammonium ion as determined by nmr integration. However, the relative intensities of the peaks in the infrared spectrum imply a ratio on the order of 3:1. [That is, the fraction is 60% adduct and 40% boronium salt, by weight.]

The infrared spectrum of the CH_2Cl_2 insoluble material (A) (Figure 11) differed from that of authentic $(CH_3)_2NHBCl_3$ in several ways. There was a peak of medium intensity at 650 cm^{-1}, probably due to BCl_4^- ion,[59] and another peak of medium intensity at 540 cm^{-1}, probably due to $amine_2BCl_2^+$. The pattern of peaks between 700-850 cm^{-1} was markedly different from the pattern in tbe spectrum of $(CH_3)_2NHBCl_3$, probably reflecting both the absence of coordinated BCl_3 groups and the presence of $amine_2BCl_2^+$ groups. There was a marked difference in the 2500-3300 cm^{-1} region also. The spectrum showed two strong,broad bands centered at 3200 cm^{-1} and 2960 cm^{-1}, and two sharp bands at 2780 cm^{-1} and 2680 cm^{-1}. These bands are probably due to the amine vibrations (N-H and C-H stretch) in $amine_2BCl_2^+$. The nmr spectrum of this fraction(A) in CD_3CN sbowed a broad, featureless absorption in the aliphatic region (157 Hz). [Exposure to atmosphere during sample preparation resulted in the appearance of a 1:2:1 triplet in the spectrum (δ = 160 Hz, J = 5.5 Hz). It would be expected that $[(CH_3)_2NH]_2BCl_2^+$ ion sbould be quite sensitive to bydrolysis.]

As conclusive proof of these assignments, an authentic sample of $[(CH_3)_2NH]_2BCl_2^+BCl_4^-$ was prepared and compared with this fraction (A).

<u>Synthesis of bis-(dimethylamine)-boronium chloride.</u> -- $[(CH_3)_2NH]_2BH_2^+Cl^-$ was prepared in a manner similar to that described by Miller and Ryschkewitsch[60] for the preparation of $[(CH_3)_2NH]_2BH_2^+I^-$. $(CH_3)_2NHBH_3$ (1.18 g, 20.0 mmol) was dissolved in 30 ml of C_6H_6 and a 0.40 N solution of HCl in C_6H_6(65 ml, 26 mmol) was added slowly with stirring. The volatiles were removed by

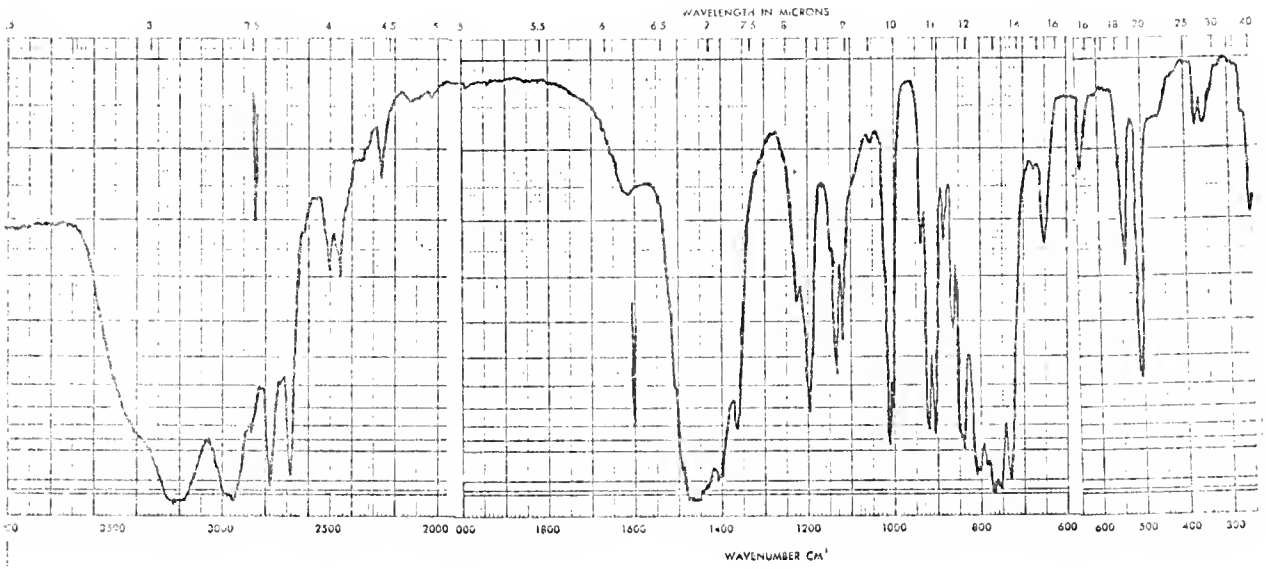

Figure 11. Infrared spectrum of fraction (A) from the reaction of $(CH_3)_2NH$ and BCl_3.

pumping, and 30 ml of fresh benzene was added to the white solid. A 1.71-N solution of $(CH_3)_2NH$ in C_6H_6 (12.0 ml, 20.5 mmol) was added with stirring. The volatiles were removed by pumping, and the white solid which remained was transferred to a tared vial. Yield of $[(CH_3)_2NH]_2BH_2^+Cl^-$ was 2.62 g (94.7%, based on $(CH_3)_2NHBH_3$), mp = 161-3°. The infrared (Figure 12) and nmr spectra were nearly identical to those observed by Miller and Rys dkewitsch[60] for $[(CH_3)_2NH]_2BH_2^+I^-$. Anal. Calcd. for $C_4H_{16}N_2BCl$: C, 34.70; H, 11.65; N, 20.23. Found: C, 33.50; H, 11.70; N, 19.73.

Synthesis of bis-(dimethylamine)-dichloroboronium chloride. -- $[(CH_3)_2NH]_2BH_2^+Cl^-$ (0.47 g, 3.40 mmol) was dissolved in 30 ml of CH_2Cl_2, and Cl_2 was bubbled in at a moderate rate for 1-1/2 hours. During the addition of Cl_2, a white solid precipitated out and the solution turned yellow. The volatiles were removed by pumping, and the white solid which remained was transferred (in the dry box) to a tared flask. The yield of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ was 0.70 g (98%, based on $[(CH_3)_2NH]_2BH_2^+Cl^-$), mp = 123.5-124°. Anal. Calcd. for $C_4H_{14}N_2BCl_3$: C, 23.17; H, 6.81; N, 13.51. Found: C, 22.72; H, 7.35; N, 12.06. The nmr spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ in CH_3CN was a broad, featureless resonance centered at 155 Hz. The infrared spectrum (Figure 13) was very similar to the spectrum of fraction (A) in the region 900-4000 cm^{-1}, but there were several differences in the region below 900 cm^{-1}, notably the absence of the peak at 650 cm^{-1} and a lower intensity of the pattern at 750-850 cm^{-1}.

Reaction of bis-(dimethylamine)-dichloroboronium chloride and boron trichloride. -- $[(CH_3)_2NH]_2BCl_2^+Cl^-$ (0.20 g, 1.0 mmol) was taken in a flask, attached to a vacuum line, and evacuated. BCl_3 (2.6 mmol) was introduced into

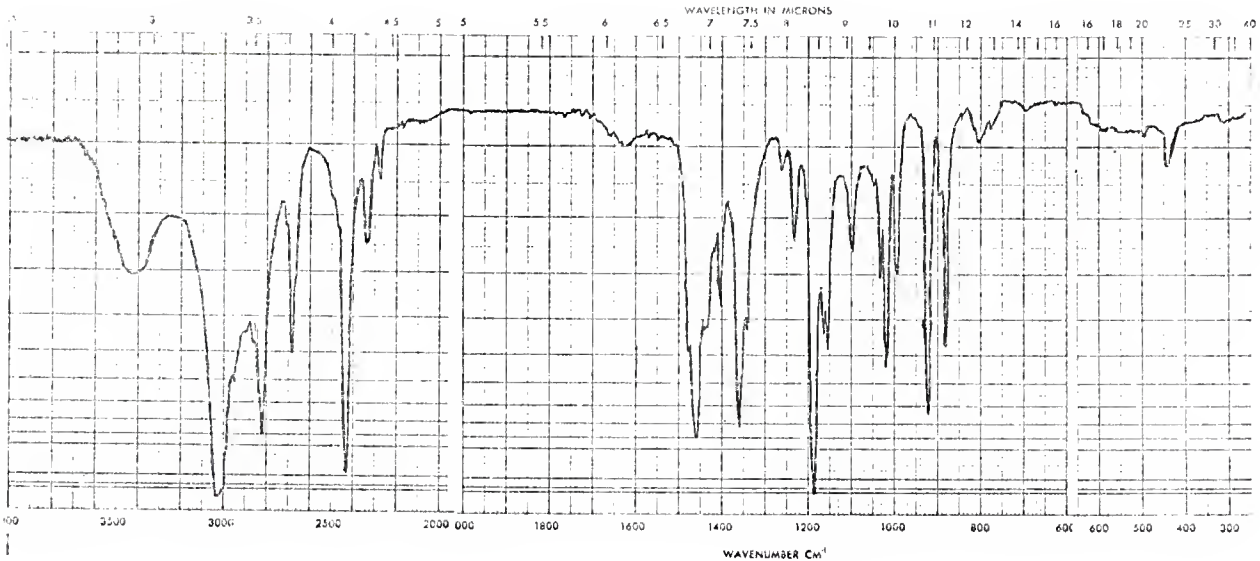

Figure 12. Infrared spectrum of $[(CH_3)_2NH_2BH_2]^+Cl^-$.

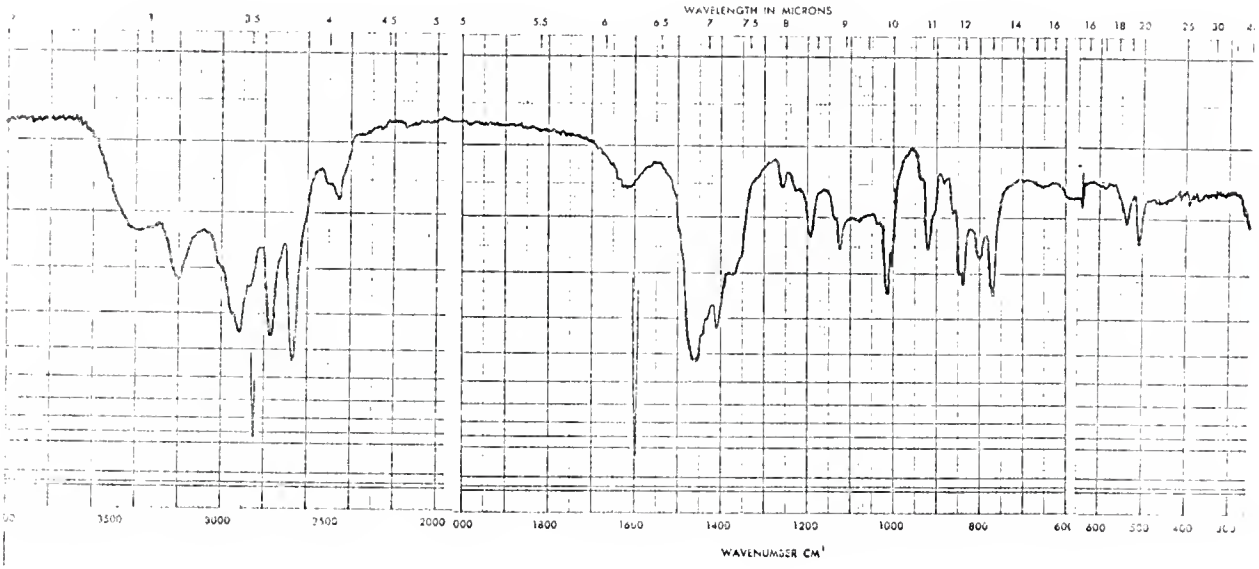

Figure 13. Infrared spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$.

the flask very slowly so that no heat buildup occurred. After the solid was exposed to all of the BCl_3, a large excess (about 20 mmol) of BCl_3 was introduced into the flask, and after one hour's exposure, the volatiles were pumped off. The white solid which remained was transferred to a tared vial. The weight of the solid was 0.275 g, corresponding to 75% conversion of Cl^- to BCl_4^-. (Since there was some material loss during transfer, the actual percentage may be as high as 80%.) The mp was 98-98.5°. The infrared spectrum of this solid (Figure 14) was identical to that of fraction (A). The new peaks in the spectrum, which are thus due to BCl_4^-, are at 650(w), 735(m), and 780(s) cm^{-1}.

In summary, the direct reaction of dimethylamine and boron trichloride produces two major products as shown in the following equation:

$$20\ (CH_3)_2NH + 20\ BCl_3 \rightarrow \begin{array}{c} 6\ (CH_3)_2NHBCl_3 \\ + \\ 7\ [(CH_3)_2NH]_2BCl_2^+BCl_4^-\ (\text{or } Cl^-) \end{array}$$

<u>Reaction of dimethylamine and boron tribromide</u>. -- Boron tribromide (3.10 ml, 36.0 mmol) was dissolved in 50 ml of dry benzene on the vacuum line (the pressure of the solution was about 100 mm). Dimethylamine (2.37 ml, 36.0 mmol) was trapped out in another part of the line and allowed to warm up. When the pressure of dimethylamine reached 500 mm, the stopcock to the BBr_3-benzene solution was opened, allowing the dimethylamine to enter at such a rate as to hold the pressure of dimethylamine in the external system steady at

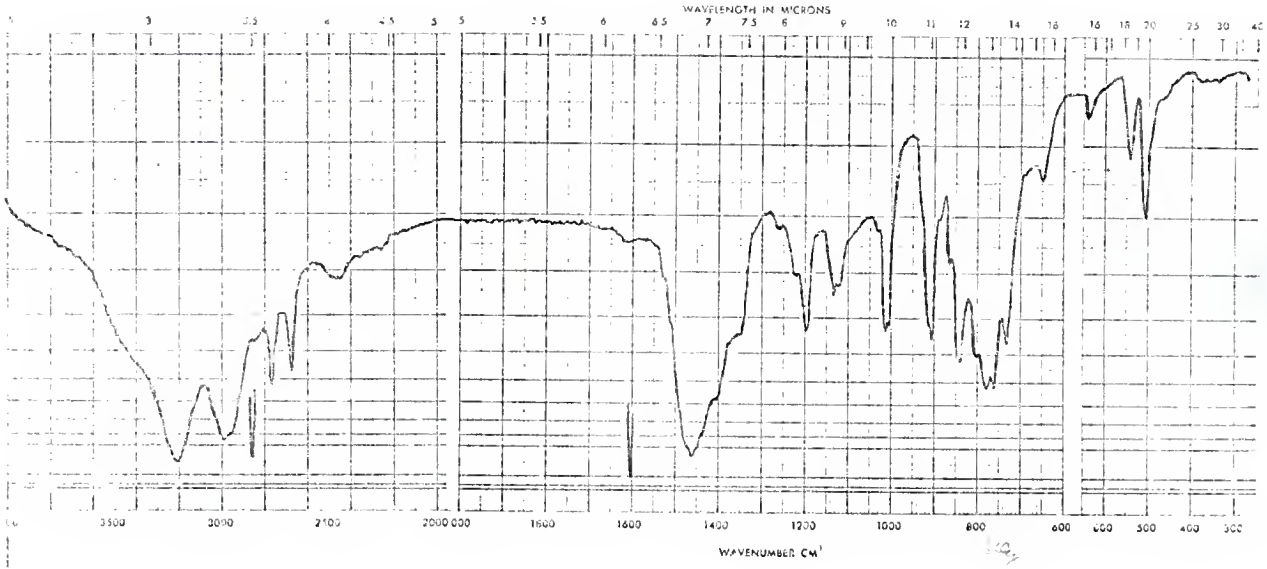

Figure 14. Infrared spectrum of $[(CH_3)_2NH]_2BCl_2^+BCl_4^-$.

500 mm; a white solid precipitated during this procedure. The addition was facilitated by stirring. After all the dimethylamine had been added, a sample of the reaction solution was taken for nmr. The spectrum showed a pattern in the aliphatic region (about 125 Hz) which appeared to be the 8-peak multiplet due to $(CH_3)_2NHBBr_3$ overlapped by a singlet possibly due to $(CH_3)_2NBBr_2$ (or some other aminoborane). The volatiles were distilled out into a liquid nitrogen trap, leaving a white solid in the flask. [An nmr spectrum of the liquid which was trapped out showed only benzene absorptions, but the liquid fumed, implying the presence of BBr_3.] After transfer to a tared vial, the product weighed 9.37 g (88% yield).

A small amount (1.0 g) of this product was stirred witb 40 ml of CH_2Cl_2 for ten bours. The solution was filtered, giving a white solid (A). The solvent was removed from the filtrate on a rotary evaporator, leaving a gray powdery solid (B). Each fraction was about half of the original material.

An nmr spectrum was taken in CH_2Cl_2 solution of the CH_2Cl_2-soluble fraction (B), which showed a complex pattern in the aliphatic region. This multiplet was the result of the overlapping of three sets of resonance: 1) an 8-peak multiplet, centered at 180 Hz, due to $(CH_3)_2NHBBr_3$, 2) a 1:2:1 triplet, centered at 171 Hz due to $(CH_3)_2NH_2^+$ (J_{HNCH} = 5.6 Hz), and 3) a singlet at 181 Hz due to $(CH_3)_2NBBr_2$. Tbe ratio of intensities of tbese three resonances (determined by estimating visually) is roughly 8:1:0.3 [$(CH_3)_2NHBBr_3$: $(CH_3)_2NH_2^+$: $(CH_3)_2NBBr_2$]. The infrared spectrum of this fraction (B) was identical to that of authentic $(CH_3)_2NHBBr_3$.

The infrared spectrum of the CH_2Cl_2 insoluble material (A) (Figure 15) was quite different from that of $(CH_3)_2NHBBr_3$. In fact, above 900 cm^{-1} the spectrum of fraction (A) is very similar to that of $[(CH_3)_2NH]_2BCl_2^+Cl^-$, implying that the material is a salt of $[(CH_3)_2NH]_2BBr_2^+$. The region below 900 cm^{-1} shows a series of bands at 650-820 cm^{-1} (maxima at 665, 685, 720, 785, and 815 cm^{-1}) due to $amine_2BBr_2^+$ vibrations. In addition, there are two bands at 450 and 470 cm^{-1} and a band at 550 cm^{-1}, due to BBr_2^+ and BBr_4^- respectively.[61] [The two bands at 450 and 470 cm^{-1} are related to two similar bands at 505 and 540 cm^{-1} in the spectrum of $[(CH_3)_2NH]_2BCl_2^+Cl^-$.] An nmr spectrum of this fraction (A) was taken in CH_3CN, which showed two resonances in the aliphatic region: 1) a broad featureless resonance (about 12 Hz wide) at 171 Hz, due to $[(CH_3)_2NH]_2BBr_2^+$ and 2) a 1:2:1 triplet at 159.5 Hz due to $(CH_3)_2NH_2^+$ (J = 5.6 Hz). However, the absence of bands in the infrared spectrum characteristic of $(CH_3)_2NH_2^+$ shows that the ammonium ion comes from hydrolysis of $[(CH_3)_2NH]_2BBr_2^+$.

In summary, the direct reaction of dimethylamine and boron tribromide produces two major products and two minor products as shown in the following equation:

$$4(CH_3)_2NH + 4BBr_3 \rightarrow \begin{array}{l} 2(CH_3)_2NHBBr_3 \\ + \\ 1[(CH_3)_2NH]_2BBr_2^+BBr_4^- \text{ (or } Br^-) \\ + \\ \ll 1[(CH_3)_2NH_2^+BBr_4^- + (CH_3)_2NBBr_2] \end{array}$$

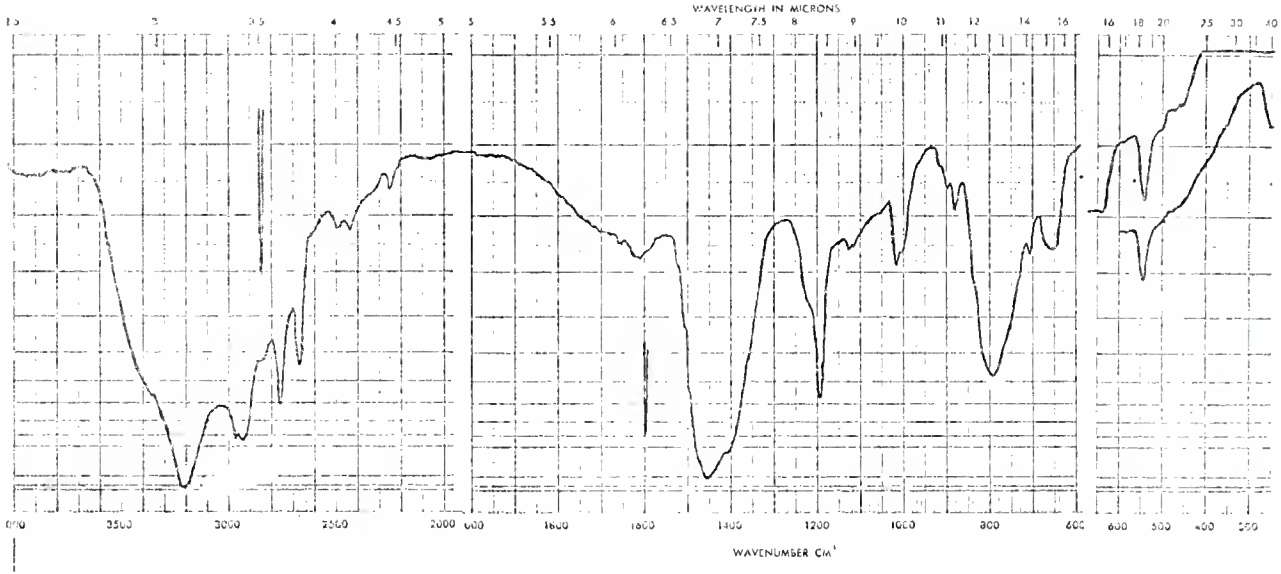

Figure 15. Infrared spectrum of fraction (A) from the reaction of $(CH_3)_2NH$ and BBr_3.

Preparation of Diethylamine-Haloboranes

Synthesis of diethylamine-borane. -- Diethylamine-borane was prepared via a transamination reaction of diethylamine with trimethylamine-borane. Trimethylamine-borane (21.4 g) was dissolved in a large excess of diethylamine (60 ml) and refluxed for about three hours. The excess diethylamine was pumped off, and the remaining diethylamine-borane, an oil, was purified by shaking with water and extracting with methylene chloride, the methylene chloride being evaporated to give a good yield (21.6 g, 85%) of liquid diethylamine-borane. Infrared and ^{1}H nmr spectra showed the compound to be free of impurities. The nmr spectrum showed a triplet in the methyl region, a quintet in the methylene region (Figure 16),and a broad resonance farther downfield, due to N-H. The chemical shifts and coupling constants are given in Table IV. The infrared spectrum (Figure 17) was characterized by a strong peak at about 3200 cm^{-1}, due to N-H stretch, and a strong doublet centered at 2350 cm^{-1}, due to coordinated BH_3 stretch.

The ^{11}B nmr spectrum of $(CH_3CH_2)_2NHBH_3$ showed a quartet (J_{BH} = 97.5 Hz) centered at 34.6 ppm upfield from trimethylborate.

Synthesis of diethylamine-monochloroborane. -- A sample of dietbylamine-borane (about 1.0 g) was dissolved in 20 ml of CH_2Cl_2, and a solution of HCl in CH_2Cl_2 was added. The nmr spectrum was monitored as the HCl solution was added, and the triplet in the methyl region due to starting material was observed to diminish in intensity as a new triplet just downfield increased in intensity. Concomitantly, a complex multiplet grew downfield from the 5-peak multiplet of starting material in the methylene region. When the triplet due to

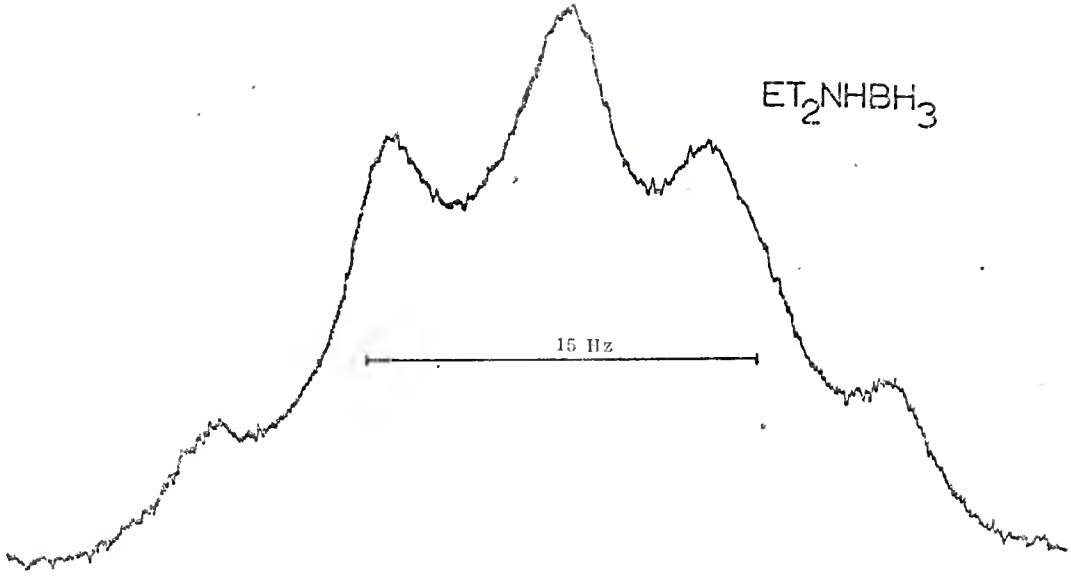

Figure 16. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBH_3$.

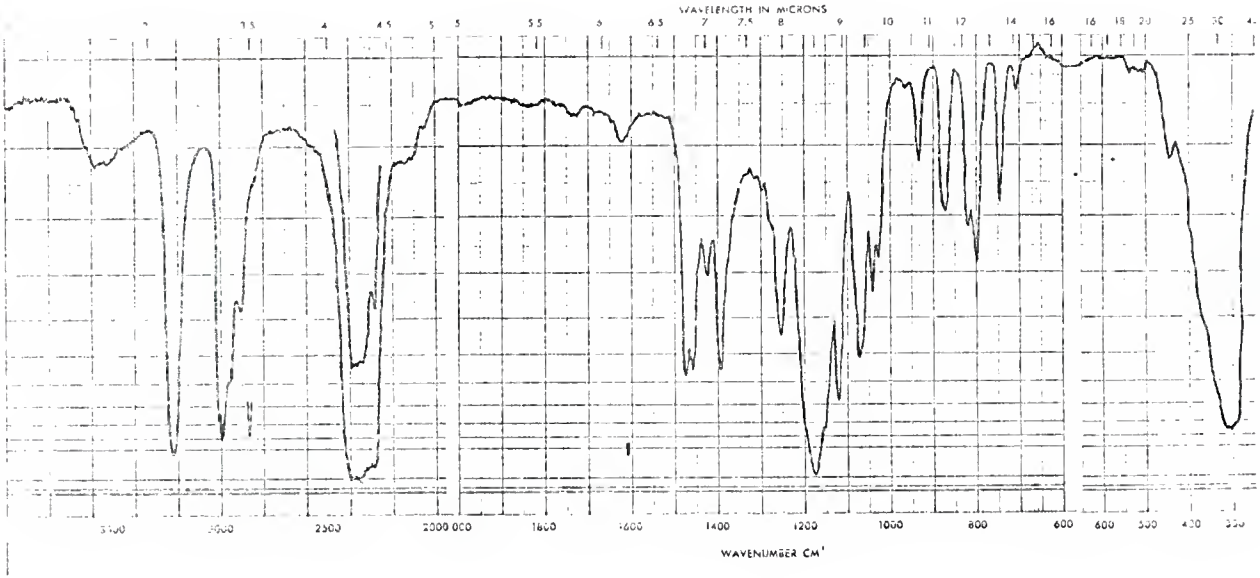

Figure 17. Infrared spectrum of $(CH_3CH_2)_2NHBH_3$.

starting material had disappeared completely, addition of HCl solution was stopped and the volatiles removed from the solution by pumping. The oil which remained in the flask was transferred to a dry box for storage. A sample of this oil was dissolved in CH_2Cl_2, and a fresh nmr was taken. This spectrum showed a triplet in the methyl region, a complex multiplet in the methylene region (Figure 18), and a broad absorption farther downfield, due to N-H resonance. The chemical shifts and coupling constants are given in Table IV. The infrared spectrum of this oil, taken between KBr plates, was consistent with the formulation $(CH_3CH_2)_2NHBH_2Cl$ (Figure 19). There was a strong peak at 3190 cm^{-1}, due to N-H stretch, and a doublet at [2450, 2370 cm^{-1}], due to BH_2 stretch. The entire infrared spectrum is given in Table I.

Synthesis of diethylamine-dichloroborane. -- A sample of diethylamine-borane (about 1.0 g) was dissolved in CH_2Cl_2 and HCl gas bubbled in at a moderate rate. The nmr spectrum of the solution taken after adding HCl for 1/2 hour showed two triplets in the methyl region and a complex multiplet in the methylene region. One of the triplets, the one farther upfield, corresponded to $(CH_3CH_2)_2NHBH_2Cl$. The other triplet was assigned to $(CH_3CH_2)_2NHBHCl_2$. The ratio of the two compounds as evidenced by the ratio of intensities of the two triplets was about 4:1, the monochloroborane adduct in excess. Addition of HCl was continued, and the nmr spectra taken at various times showed the triplet due to monochloroborane adduct diminish as the triplet due to dichloroborane adduct increased (no new triplet appeared during the course of this reaction). After about 4 hours, only the triplet due to dichloroborane adduct

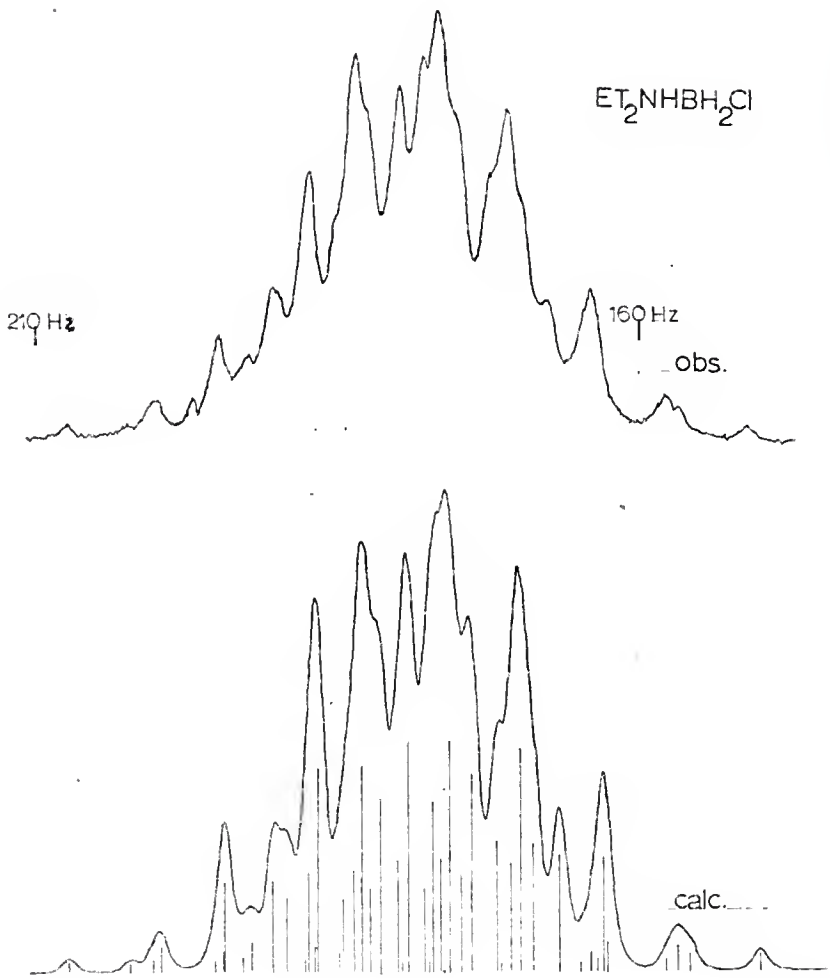

Figure 18. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBH_2Cl$.

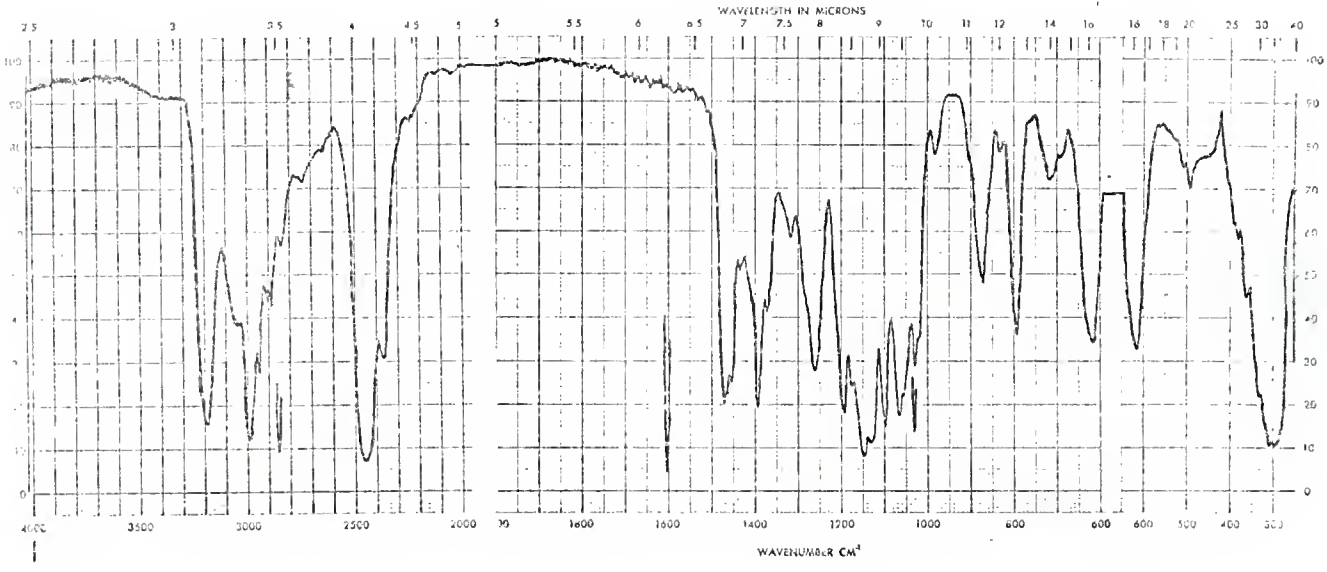

Figure 19. Infrared spectrum of $(CH_3CH_2)_2NHBH_2Cl$.

remained. The volatiles were removed from the solution by pumping and the oil which remained was taken into the dry box for storage.

A sample of this oil was dissolved in CH_2Cl_2, and a fresh nmr was taken. This spectrum showed a triplet in the methyl region, a complex multiplet in the methylene region (Figure 20), and a broad absorption farther downfield, due to N-H resonance. The chemical shifts and coupling constants are given in Table IV. The infrared spectrum of this oil, taken between KBr plates, was consistent with the formulation $(CH_3CH_2)_2NHBHCl_2$ (Figure 21). There was a strong peak at 3200 cm^{-1}, due to N-H stretch, and a single strong peak at 2500 cm^{-1}, due to B-H stretch. The entire infrared spectrum is given in Table I.

Synthesis of diethylamine-trichloroborane. -- A sample of diethylamine-borane (about 0.5 g) was dissolved in 25 ml of CH_2Cl_2 and chlorine gas bubbled in until a permanent yellow color was imparted to the solution. The volatiles were removed by a stream of nitrogen, leaving a white solid, mp = 129-130°. Anal. Calcd. for $C_4H_{11}NBCl_3$: C, 25.25; H, 5.83; N, 7.36. Found: C, 25.46; H, 6.01; N, 7.22.

The nmr spectrum of $(CH_3CH_2)_2NHBCl_3$ in CH_2Cl_2 consisted of a triplet in the methyl region and a complex multiplet in the methylene region (Figure 22). The chemical shifts and coupling constants are given in Table IV. The infrared spectrum of $(CH_3CH_2)_2NHBCl_3$ (Figure 23) was characterized by a strong peak at 3190 cm^{-1}, due to N-H stretch, and by the absence of B-H stretching absorptions in the region 2300-2500 cm^{-1}. The entire infrared spectrum is given in Table I.

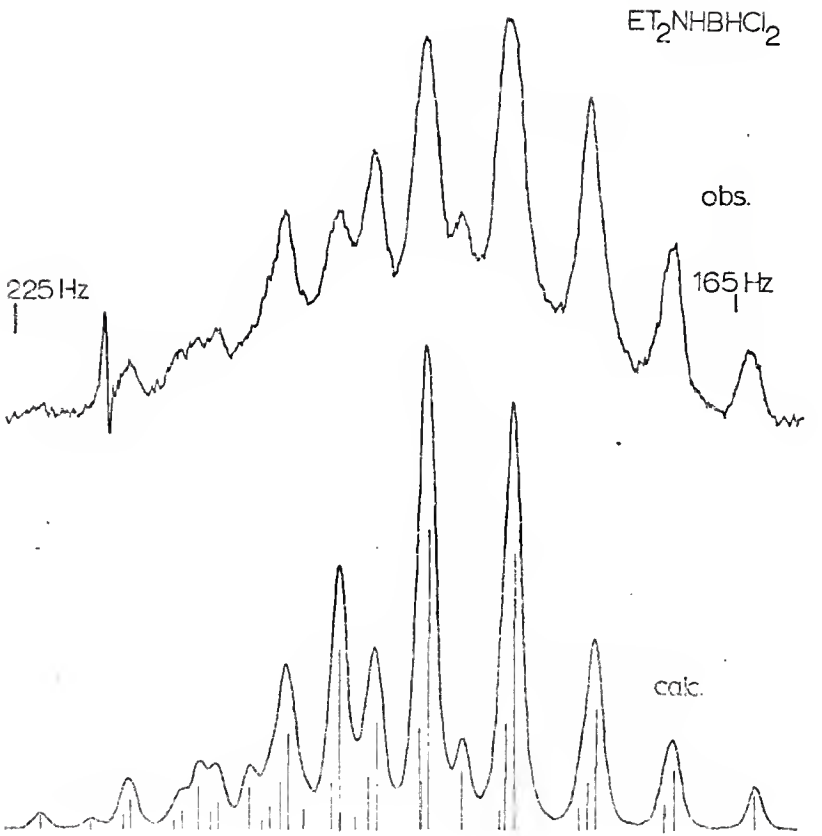

Figure 20. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBHCl_2$.

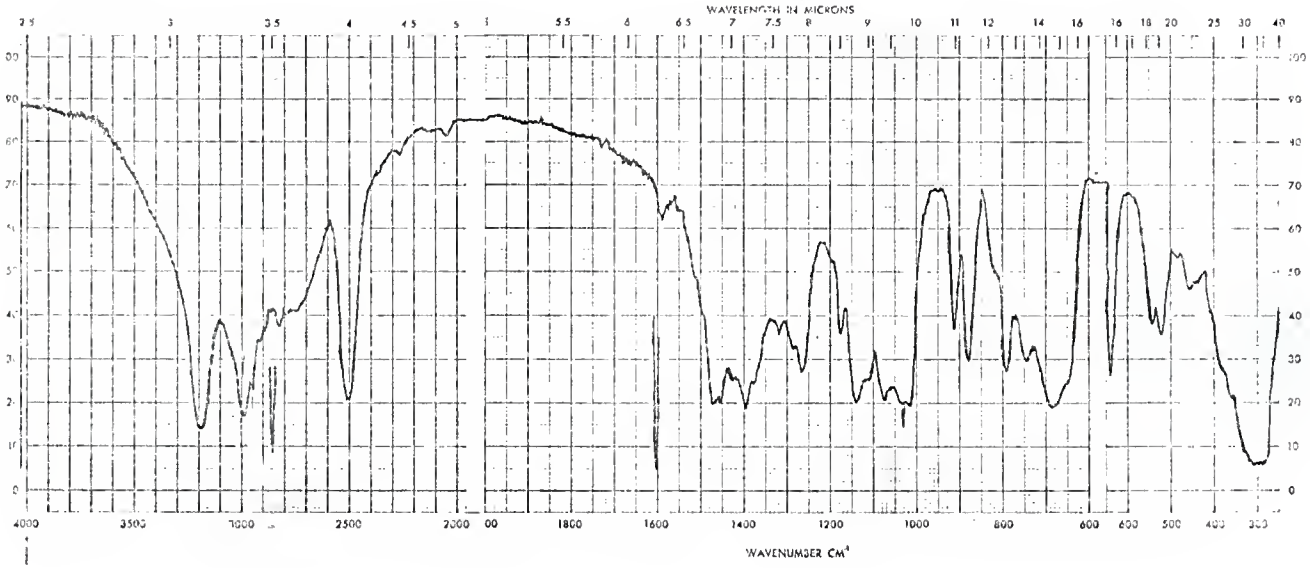

Figure 21. Infrared spectrum of $(CH_3CH_2)_2NHBHCl_2$.

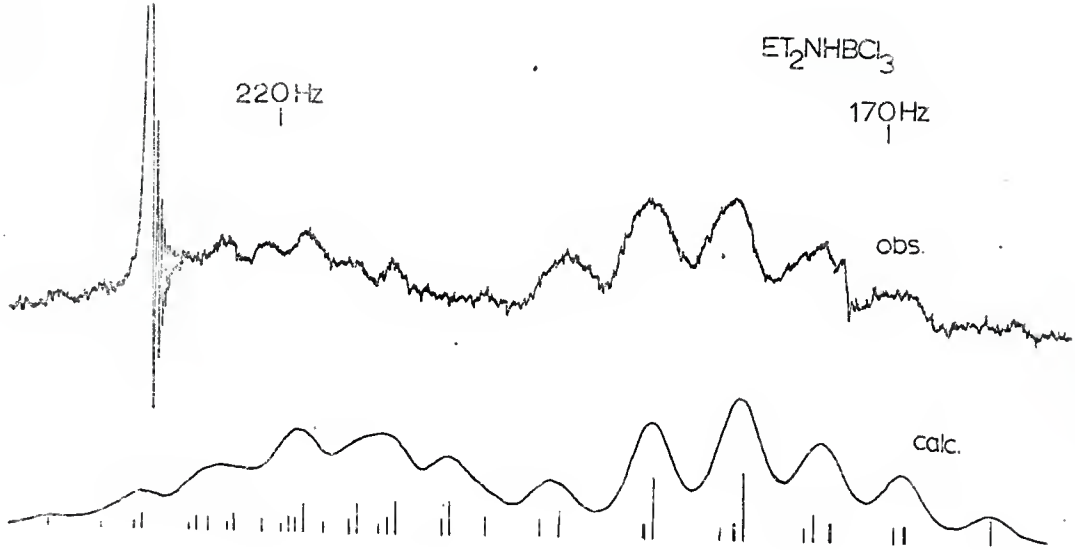

Figure 22. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBCl_3$.

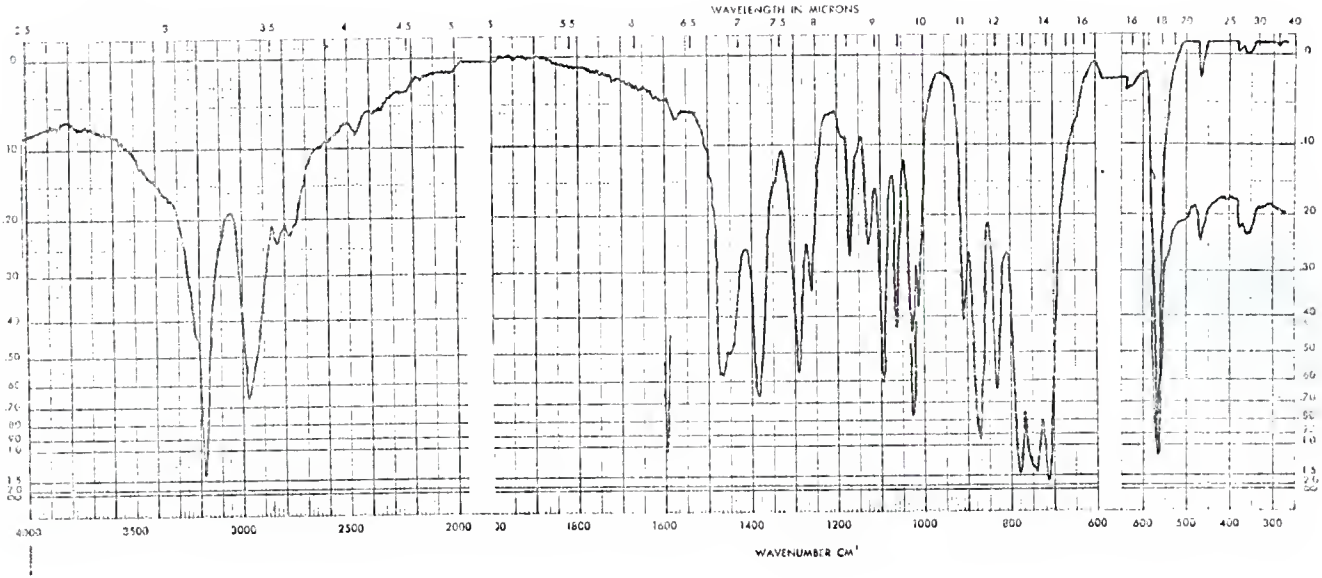

Figure 23. Infrared spectrum of $(CH_3CH_2)_2NHBCl_3$.

Reaction of diethylamine-borane and hydrogen bromide. -- Diethylamine-borane (0.577 g, 6.64 mmol) was dissolved in CH_2Cl_2, and a 0.33 M solution of HBr in CH_2Cl_2 (20.0 ml, 6.60 mmol) was added with stirring. The nmr spectrum of the solution consisted of a triplet in the methyl region, just downfield from the position of the triplet of the starting material, a complex multiplet in the methylene region (Figure 24), and a broad absorption farther downfield, due to N-H resonance. This pattern was assigned to $(CH_3CH_2)_2NHBH_2Br$. Addition of excess HBr caused the peaks due to $(CH_3CH_2)_2NHBH_2Br$ to diminish, being replaced by a new triplet and complex multiplet downfield from those of $(CH_3CH_2)_2NHBH_2Br$. The new peaks were assigned to $(CH_3CH_2)_2NHBHBr_2$.

Reaction of diethylamine-borane and bromine. -- Diethylamine-borane (0.432 g, 4.97 mmol) was dissolved in 25 ml of CH_2Cl_2. Bromine (0.791 g, 4.95 mmol) dissolved in 2 ml of CH_2Cl_2 was added to the amine-borane solution dropwise with stirring. The nmr spectrum of the resulting solution showed two sets of triplets in the methyl region, of relative intensity 5:1, the positions of which correspond to the previously assigned $(CH_3CH_2)_2NHBHBr_2$ and $(CH_3CH_2)_2NHBH_2Br$, respectively. More bromine (0.132 g, 0.83 mmol) was added as a CH_2Cl_2 solution and another nmr spectrum taken. The spectrum showed only the triplet due to $(CH_3CH_2)_2NHBHBr_2$ in the methyl region. In addition, there was a complex multiplet in the methylene region (Figure 25) and a broad absorption due to N-H resonance farther downfield. The chemical shifts and coupling constants for these two adducts are given in Table IV.

The ^{11}B nmr spectrum of $(CH_3CH_2)_2NHBHBr_2$ showed a broad (400 Hz wide) featureless resonance at 22.8 ppm upfield from trimethylborate.

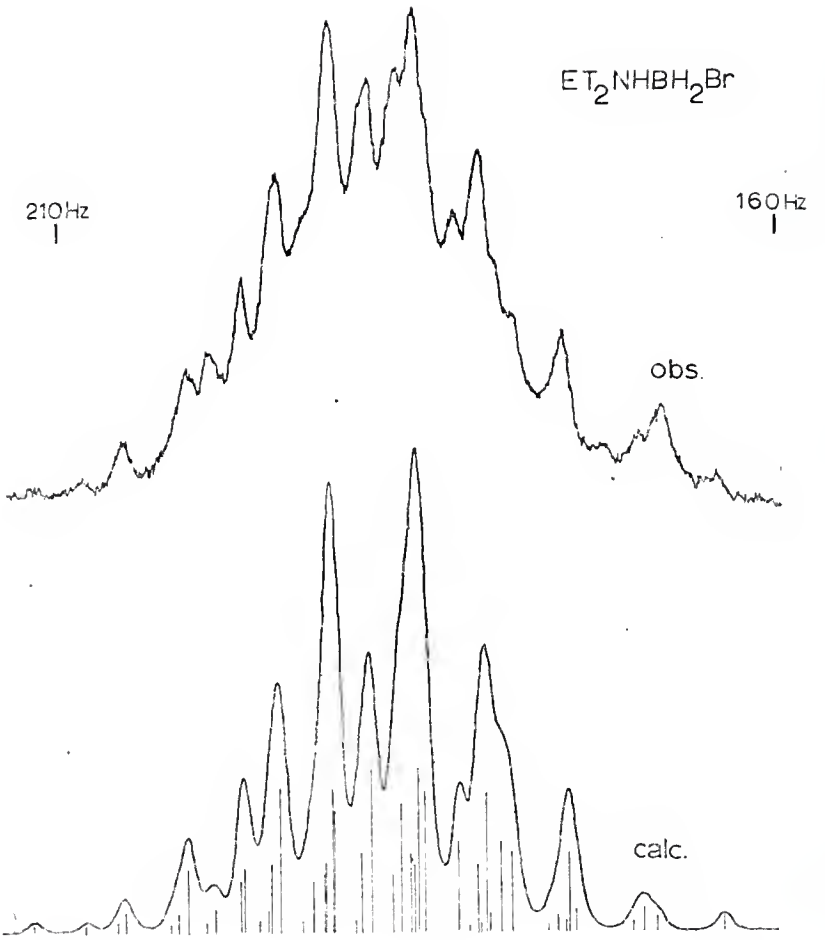

Figure 24. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBH_2Br$.

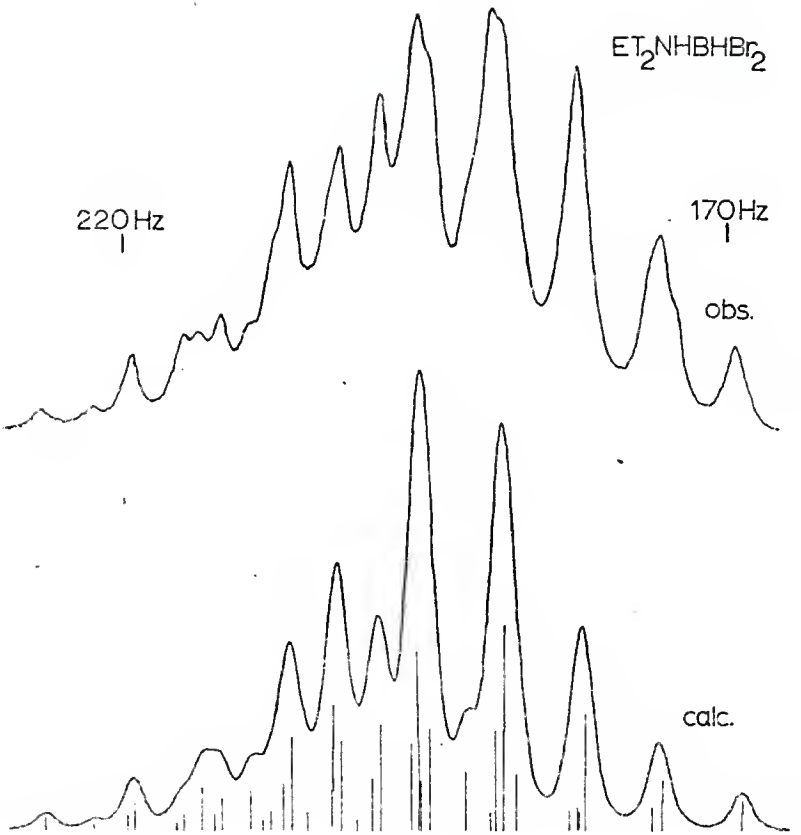

Figure 25. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBHBr_2$.

Synthesis of diethylamine-tribromoborane. -- Diethylamine-borane (about 0.8 g) was dissolved in CH_2Cl_2 and bromine added slowly with stirring until a permanent color was imparted to the solution. The volatiles were evaporated by a stream of nitrogen, leaving a light yellow solid, mp = 155-157°. Anal. Calcd. for $C_4H_{11}NBBr_3$: C, 14.84; H, 3.43; N, 4.33. Found: C, 15.28; H, 3.60; N, 4.27.

The nmr spectrum of $(CH_3CH_2)_2NHBBr_3$ in CH_2Cl_2 consisted of a triplet in the methyl region and a complex multiplet in the methylene region (Figure 26). The chemical shifts and coupling constants are given in Table IV. The infrared spectrum of $(CH_3CH_2)_2NHBBr_3$ (Figure 27) was characterized by a strong peak at 3180 cm^{-1}, due to N-H stretch, and by the absence of B-H stretching absorptions in the region 2300-2500 cm^{-1}. The entire infrared spectrum is given in Table I.

The ^{11}B nmr spectrum showed a single peak at 24.9 ppm upfield from trimethylborate.

Synthesis of diethylamine-monoiodoborane. -- Diethylamine-borane (0.985 g, 11.3 mmol) was dissolved in 30 ml of CH_2Cl_2, and iodine (1.44 g, 5.67 mmol) was added piecewise with stirring. The volatiles were removed from the resulting solution by pumping, leaving a colorless, viscous oil, which was taken into the dry box for storage. Yield was 1.950 g (80.5%, based on $(CH_3CH_2)_2NHBH_3$).

A sample of this oil was dissolved in CH_2Cl_2, and an nmr spectrum obtained. The spectrum showed a triplet in the methyl region, a complex multiplet in the methylene region (Figure 28), and a broad absorption due to

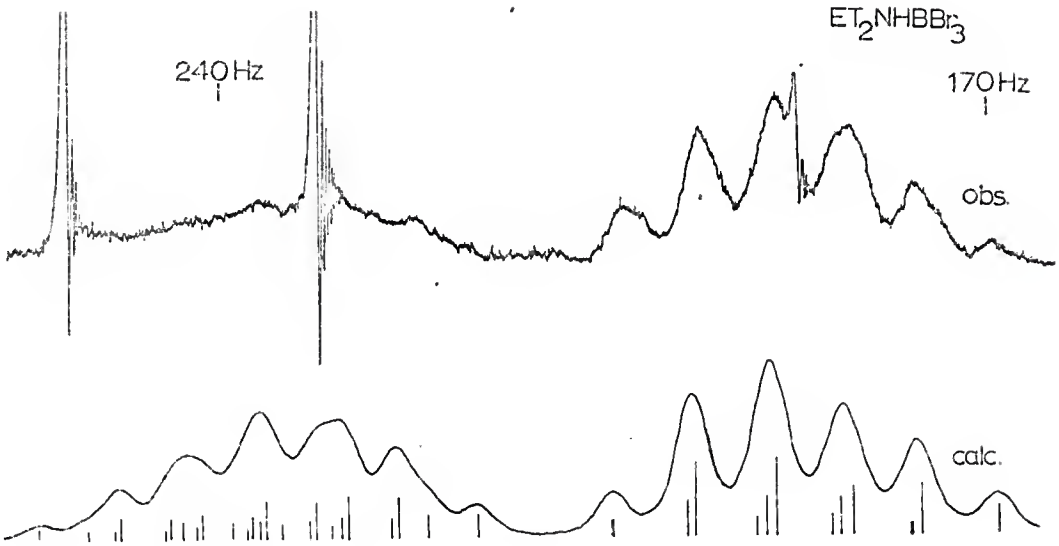

Figure 26. Methylene region of the ^{1}H nmr spectram of $(CH_3CH_2)_2NHBBr_3$.

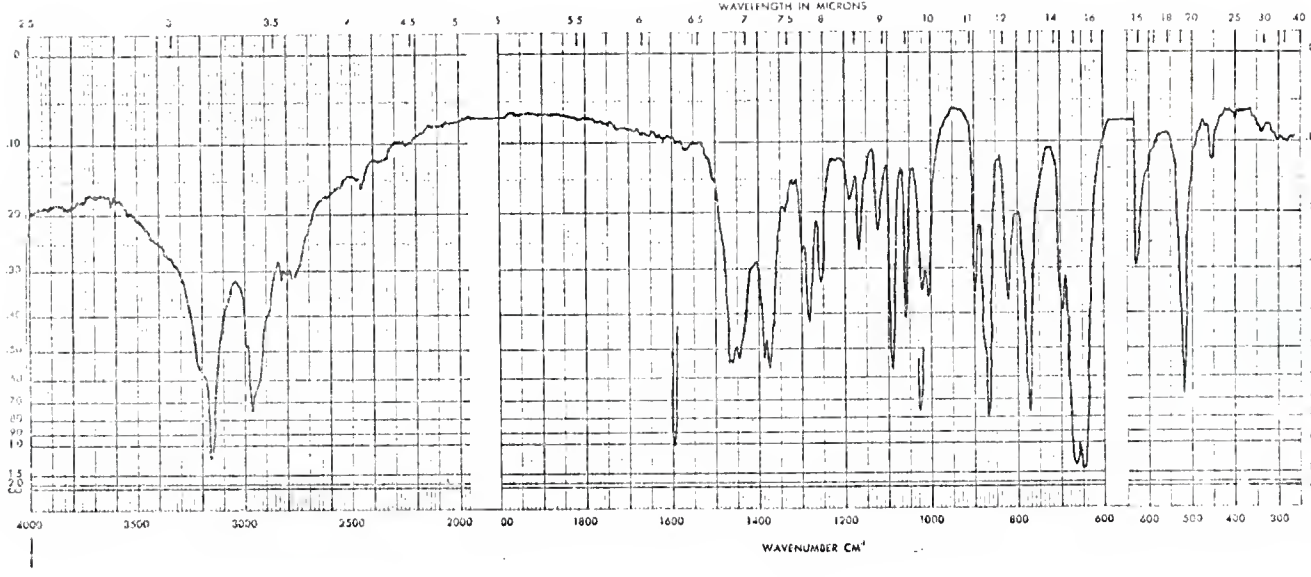

Figure 27. Infrared spectrum of $(CH_3CH_2)_2NHBBr_3$.

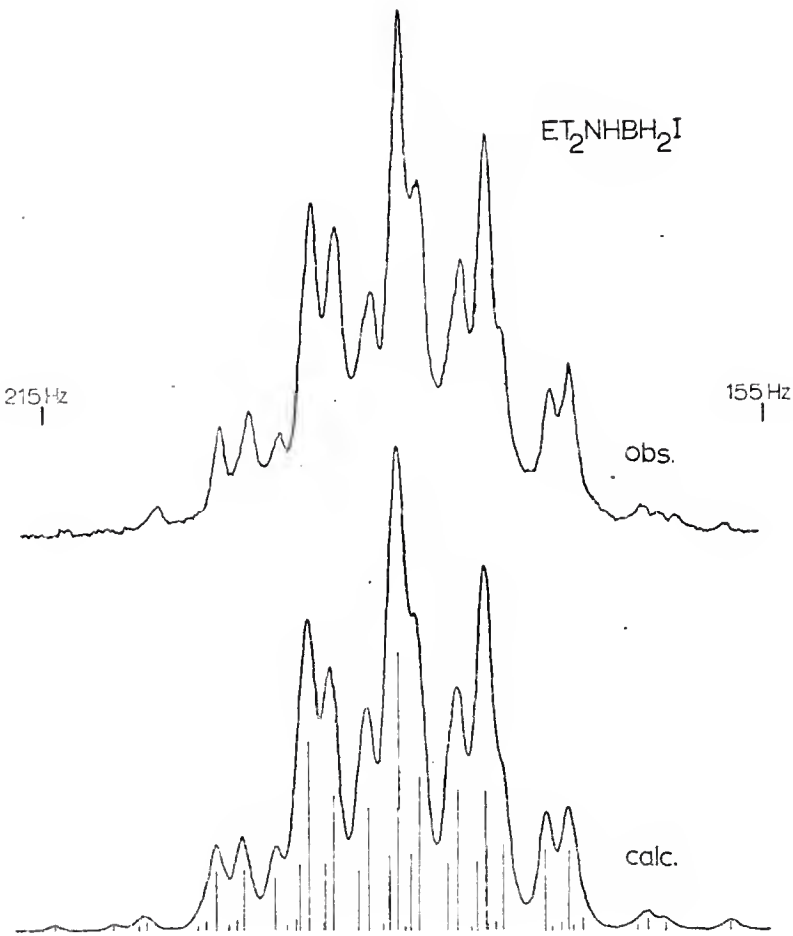

Figure 28. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBH_2I$.

N-H resonance farther downfield. The chemical shifts and coupling constants are given in Tahle IV. The infrared spectrum of $(CH_3CH_2)_2NHBH_2I$ (Figure 29) was taken, hetween KBr plates, and was characterized by a strong peak at 3140 cm^{-1}, due to N-H stretch, and a doublet at [2450, 2500 cm^{-1}], due to B-H stretch. The entire infrared spectrum is given in Table I.

Reaction of diethylamine-horane and iodine. -- Diethylamine-borane (0.840 g, 9.66 mmol) was dissolved in 30 ml of CH_2Cl_2. Iodine (2.46 g, 9.70 mmol) was added piecewise with stirring. The nmr spectrum of the solution taken 3 hours after all the iodine had been added showed two sets of triplets in the methyl region (in a ratio of ahout 6:1). The triplet of lower intensity and farther upfield was in the same position as the triplet of $(CH_3CH_2)_2NHBH_2I$; therefore, the other triplet was assigned to $(CH_3CH_2)_2NHBHI_2$. The nmr spectrum taken after 20 hours showed, in the methyl region, the same two triplets in a ratio of 20:1, $(CH_3CH_2)_2NHBHI_2$ in excess. The nmr spectrum after 60 hours showed, in the methyl region, only the triplet due to $(CH_3CH_2)_2NHBHI_2$. The complete nmr spectrum of $(CH_3CH_2)NHBHI_2$ consisted of a triplet in the methyl region, a complex multiplet in the methylene region (Figure 30), and a broad absorption farther downfield, due to N-H resonance. The chemical shifts and coupling constants are given in Table IV.

In another experiment, diethylamine-borane (0.812 g, 9.34 mmol) was dissolved in 75 ml of C_6H_6 in a 125 ml flask fitted with a condenser. The system was protected from the atmosphere by a stream of N_2 through a T-tube ahove the condenser. Iodine (7.00 g, 27.6 mmol) was added piecewise with stirring until a permanent color was imparted to the solution, then the rest of the iodine

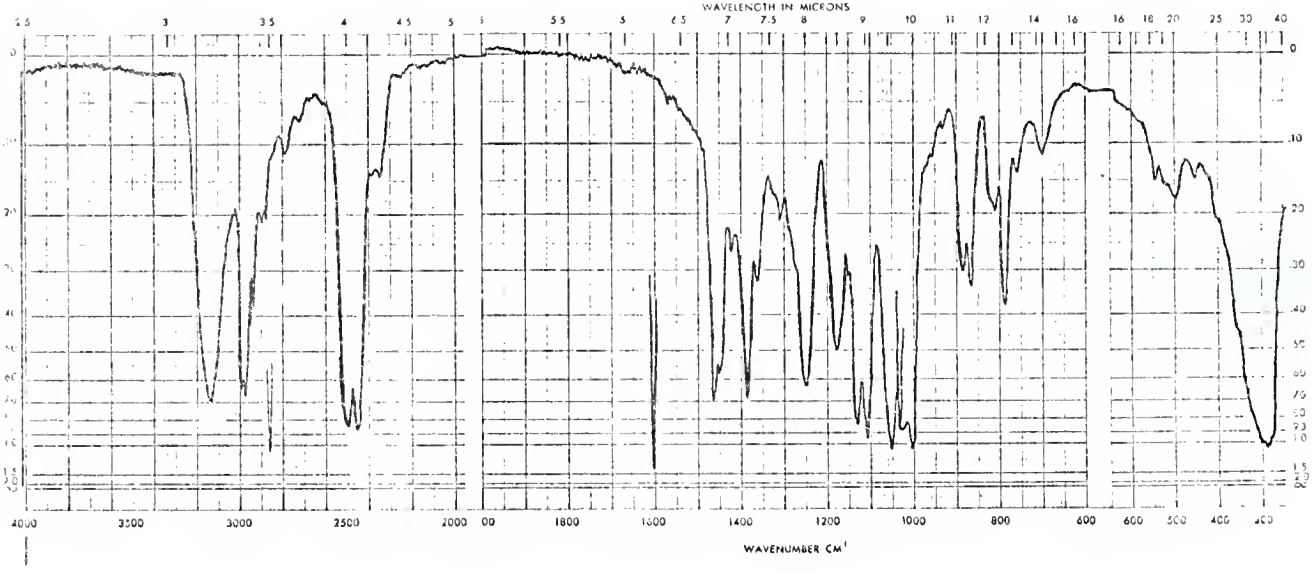

Figure 29. Infrared spectrum of $(CH_3CH_2)_2NHBH_2I$.

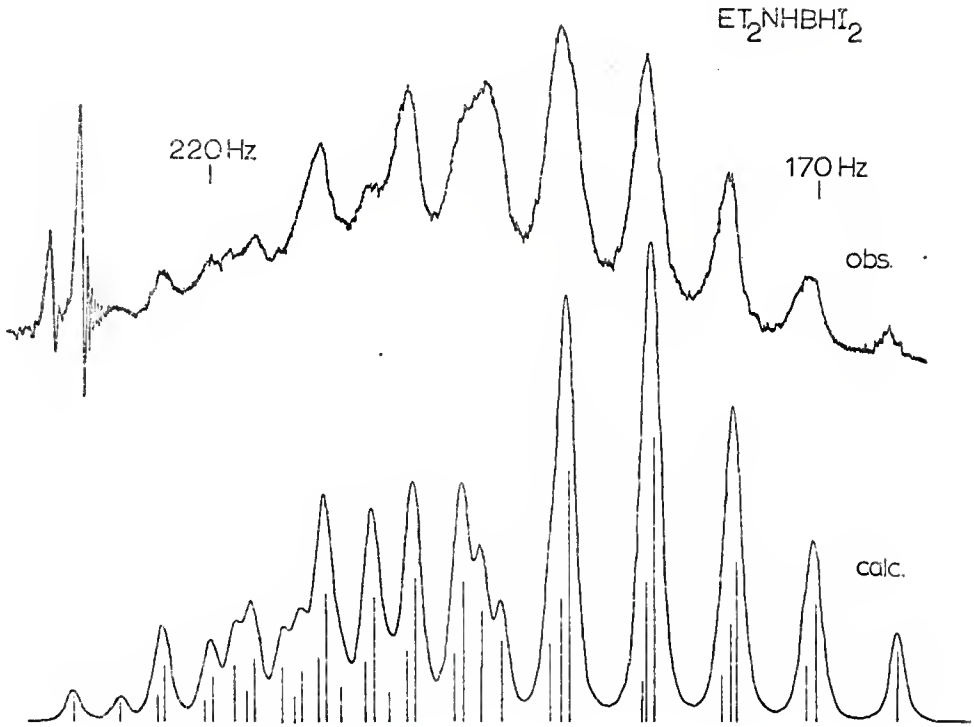

Figure 30. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBHI_2$.

was added and the flask heated until the solution was brought to a gentle reflux. After 15 bours of reflux, the nmr spectrum of tbe solution showed two triplets in the methyl region in a ratio of about 3:1, and in the methylene region, a quartet overlapping an unresolved absorption. After 40 hours of reflux, the nmr spectrum showed only a triplet in the position of the triplet which was more intense in the previous spectrum, and a quartet in the metbylene region, in the same position in the quartet in the previous spectrum. Tbe ratio of intensity was 39:62 (or about 4:6) and the pattern was assigned to $(CH_3CH_2)_2NH_2^+$ ion, the coupling of NH_2 to CH_2 being lost because of rapid exchange of the N-H protons.

Reaction of diethylamine and boron trifluoride-etherate. -- A solution of diethylamine in ether was added dropwise to an etber solution of boron trifluoride-etberate. Evaporation of the volatiles left low-melting, colorless crystals of diethylamine-trifluoroborane. On standing in air these crystals decomposed to a brown oil. An nmr spectrum of this material in CH_2Cl_2 solution showed a triplet in the methyl region, a complex, unanalyzable multiplet in the methylene region (Figure 31),and a broad absorption farther downfield, due to N-H resonance. The chemical shifts and coupling constants, where assignable, are given in Table IV.

Reaction of N-Deuterodimethylamine-Borane with Various Halogenating Agents

Syntbesis of N-deuterodimethylamine-borane. -- A sample of dimethylamine-borane (about 5 g) was added to 40 ml of D_2O and stirred for 2 bours, during which time most of the borane dissolved. The borane was extracted from the D_2O with two 40-ml portions of methylene chloride, using a 125-ml

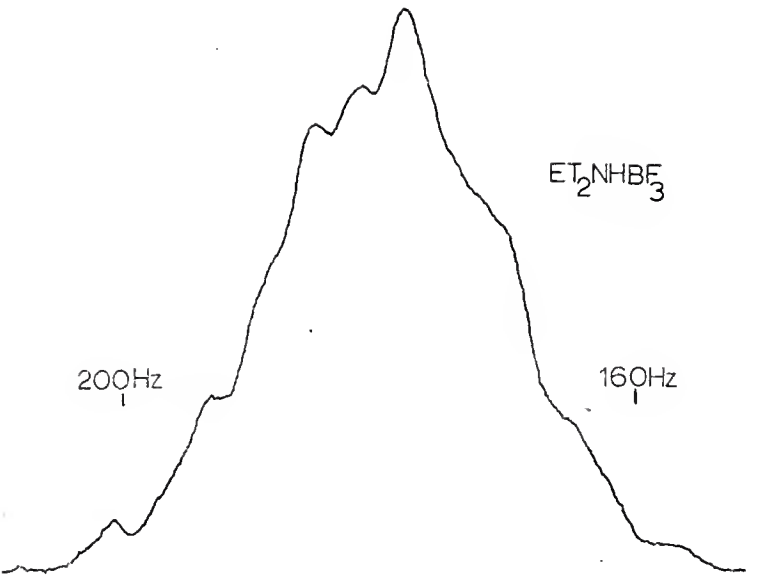

Figure 31. Methylene region of the ^{1}H nmr spectrum of $(CH_3CH_2)_2NHBF_3$.

separatory funnel. The resulting solution was dried over Na_2CO_3 overnight, then filtered and pumped to dryness. A white crystalline solid remained, mp = 34.5-35.5° [literature[62] for $(CH_3)_2NHBH_3$ = 36°]. The nmr spectrum in CH_2Cl_2 showed a single peak at 151.5 Hz, downfield from internal tetramethylsilane (TMS). The infrared spectrum was identical to that of authentic $(CH_3)_2NDBH_3$ prepared from N-deuterodimethylammonium chloride and lithium borohydride.[33]

Reaction of N-deuterodimethylamine-borane and chlorine. -- A sample of $(CH_3)_2NDBH_3$ (about 0.05 g) was dissolved in 20 ml of CH_2Cl_2, and Cl_2 gas was bubbled in until the solution turned yellow. (The rate of addition was such that the color change occurred within 10 minutes.) Volatiles were removed by pumping, and a white solid remained. The nmr spectrum of this solid in CH_2Cl_2 solution showed a six-peak multiplet centered at 174.5 Hz, downfield from internal TMS, with an intensity ratio of about 1:3:4:4:3:1. The infrared spectrum of this solid showed peaks at 3200 cm^{-1} (N-H stretch) and at 2400 cm^{-1} (N-D stretch) in a ratio of about 1:1, in addition to the pattern for $(CH_3)_2NHBCl_3$. (There was an extra peak at 970 cm^{-1}.) Thus this solid was a mixture of $(CH_3)_2NHBCl_3$ and $(CH_3)_2NDBCl_3$ in a 1:1 ratio.

Note that the nmr pattern expected for $(CH_3)_2NDBCl_3$ is a 1:1:1:1 quartet, with peaks coincident with the 2nd, 3rd, 4th, and 5th peaks of the $(CH_3)_2NHBCl_3$ sextet.

Reaction of N-deuterodimethylamine-borane and bromine. -- A sample of $(CH_3)_2NDBH_3$ (about 0.05 g) was dissolved in 25 ml of CH_2Cl_2, and Br_2 was added dropwise with stirring until the solution turned yellow. The time of

addition was about 15 minutes. Volatiles were removed by pumping, leaving a white solid. The nmr spectrum of this solid in CH_2Cl_2 solution showed a quartet (1:1:1:1) with two small peaks, one just upfield and one just downfield of the quartet. This pattern was centered at 182.5 Hz, downfield from internal TMS. The infrared spectrum of this solid showed peaks at 3150 cm^{-1} (N-H stretch) and 2350 cm^{-1} (N-D stretch) in a ratio of about 1:9, in addition to the pattern for $(CH_3)_2NHBBr_3$. (There were extra peaks at 870 cm^{-1} and 960 cm^{-1}.) Thus the solid was a mixture of $(CH_3)_2NHBBr_3$ and $(CH_3)_2NDBBr_3$ in 1:9 ratio.

Reaction of N-deuterodimethylamine-borane and iodine. -- A sample of $(CH_3)_2NDBH_3$ (0.0255 g, 0.432 mmol) was dissolved in 5 ml of CH_2Cl_2 and I_2 (0.0553 g, 0.218 mmol) added piecewise with stirring. The nmr spectrum of the resulting solution showed one peak at 165 Hz, downfield from internal TMS, with no fine structure. Thus the product was $(CH_3)_2NDBH_2I$.

A sample of $(CH_3)_2NDBH_3$ (0.1098 g, 1.83 mmol) was dissolved in 15 ml of CH_2Cl_2. I_2 (0.7003 g, 2.73 mmol) was added and the solution stirred. The nmr spectrum of the solution after 7 hours of stirring showed one peak, with no fine structure, at 173 Hz, downfield from internal TMS. Thus the product was $(CH_3)_2NDBHI_2$.

Reaction of N-deuterodimethylamine-borane and hydrogen chloride.-- A sample of $(CH_3)_2NDBH_3$ (about 0.05 g) was dissolved in 25 ml of CH_2Cl_2, and HCl gas was bubbled in for 30 minutes. The HCl was thus present in large excess. The volatiles were removed immediately thereafter by pumping, leaving a gummy solid. The nmr spectrum of this solid in CH_2Cl_2 showed a 3-peak

multiplet centered at 157 Hz, downfield from internal TMS, which appeared to be a strong singlet overlapping a doublet. The singlet is thus assigned to $(CH_3)_2NDBH_2Cl$ and the doublet to $(CH_3)_2NHBH_2Cl$. The ratio of these two compounds, as estimated visually, was about 1:3, the deuterated compound in excess.

Reaction of N-deuterodimethylamine-borane with hydrogen chloride and chlorine. -- A sample of $(CH_3)_2NDBH_3$ (about 0.05 g) was dissolved in 20 ml of CH_2Cl_2. Both HCl gas and Cl_2 gas were bubbled into the solution, the rate of addition being such that the HCl was added in about a 10-fold excess over the Cl_2. After about 7 minutes of addition, the solution turned yellow, whereupon the addition of gases was stopped and the volatiles removed by pumping, leaving a white solid. The nmr and infrared spectra of this solid were nearly identical in pattern and intensity to that of the solid formed by reaction of $(CH_3)_2NDBH_3$ with Cl_2 alone. Thus, the incorporation of hydrogen on nitrogen as the result of reaction of $(CH_3)_2NDBH_3$ with Cl_2 is not affected by the presence of HCl in excess.

Reaction of N-deuterodimethylamine-borane with deuterium chloride and chlorine. -- A sample of $(CH_3)_2NDBH_3$ (about 0.05 g) was dissolved in 25 ml of CH_2Cl_2. Both DCl gas and Cl_2 gas were bubbled into the solution, the rate of addition being such that the DCl was added in about a 10-fold excess over the Cl_2. (The DCl was produced from the hydrolysis of benzoyl chloride by D_2O as described in reference 63. The benzoyl chloride was heated for about 45 minutes to drive off any HCl produced as a result of hydrolysis by H_2O impurity. D_2O (99.5%) was then added, and the resulting DCl was used only after a good stream

of gas was produced. Thus the purity of DCl was 99% or beter.) After about 20 minutes of addition, the solution turned yellow, whereupon tbe addition of gases was stopped and the volatiles removed by pumping, leaving a white solid. The nmr spectrum of this solid in CH_2Cl_2 solution showed a six-peak multiplet in the same position as that observed for the product of the reaction of $(CH_3)_2NDBH_3$ with Cl_2 alone, but the intensity ratios were quite different. The outside two peaks had lost intensity while the 2nd and 5th peaks had gained intensity. The infrared spectrum of this solid showed peaks for N-H stretch (3200 cm^{-1}) and N-D stretch (2400 cm^{-1}), but the relative intensity was about 1:3, the N-D peak being tbe stronger. Thus, incorporation of bydrogen on nitrogen as the result of reaction of $(CH_3)_2NDBH_3$ with Cl_2 is greatly retarded by the presence of DCl in excess.

Reaction of N-deuterodimetbylamine-borane and hydrogen chloride at low temperature and the synthesis of N-deuterodimethylamine-mono- and dichloroborane. -- A sample of $(CH_3)_2NDBH_3$ (about 0.05 g) was dissolved in 8 ml of CH_2Cl_2 and the solution cooled to about -78° by immersion in a dry ice/acetone bath. HCl gas was bubbled into this solution for 10 minutes, then nitrogen gas was bubbled in for 30 minutes to remove excess HCl. After warming to room temperature, the nmr spectrum of this solution was obtained, which showed one peak with no fine structure at 157 Hz, downfield from internal TMS. An infrared spectrum of the solute was obtained by using matched NaCl liquid cells with CH_2Cl_2 as a standard. This infrared spectrum showed no peak at 3200 cm^{-1}, indicating the absence of N-H. Thus the product was $(CH_3)_2NDBH_2Cl$.

In another experiment, the solution of $(CH_3)_2NDBH_2Cl$ and HCl at -78° was allowed to warm up to room temperature without removing HCl beforehand. Thus $(CH_3)_2NDBH_2Cl$ was exposed to HCl at room temperature. The nmr spectrum of this solution after 20 minutes at room temperature showed no fine structure on the singlet due to $(CH_3)_2NDBH_2Cl$. Thus there was no exchange between $(CH_3)_2NDBH_2Cl$ and HCl at room temperature within 20 minutes.

In another experiment, a sample of $(CH_3)_2NDBH_3$ (about 0.05 g) was dissolved in 8 ml of CH_2Cl_2 and cooled to -78° by immersion in a dry ice/acetone bath. HCl was bubbled in at a moderate rate for 50 minutes. The resulting solution was then allowed to stand, in a dry ice/acetone bath, and the nmr spectrum was taken from time to time. The nmr spectrum after 8-1/2 hours showed two singlets, one at 157 Hz [$(CH_3)_2NDBH_2Cl$] and one at 163 Hz [$(CH_3)_2NDBHCl_2$], downfield from internal TMS. The ratio of products was about 3:1, the dichloro adduct in excess. After 21 hours the spectrum showed a ratio of about 9:1 for $(CH_3)_2NDBHCl_2$: $(CH_3)_2NDBH_2Cl$. There was still no fine structure on the peak due to $(CH_3)_2NDBHCl_2$. After 32 hours the spectrum showed only $(CH_3)_2NDBHCl_2$. An infrared spectrum was run on this solution in matched NaCl liquid cells with CH_2Cl_2 as a standard. This infrared spectrum showed no peak at 3200 cm^{-1}. Thus the product was $(CH_3)_2NDBHCl_2$.

A portion of the solution of $(CH_3)_2NDBHCl_2$ and HCl at -78° as prepared above was allowed to warm up to room temperature without removing excess HCl beforehand. The nmr spectrum of this solution after 20 minutes at room temperature showed no fine structure on the singlet due to $(CH_3)_2NDBHCl_2$.

Thus there was no exchange between $(CH_3)_2NDBHCl_2$ and HCl at room temperature within 20 minutes.

Reaction of N-deuterodimethylamine-monochloroborane and chlorine. -- A solution of $(CH_3)_2NDBH_2Cl$ was prepared as described above, the excess HCl gas having been removed by bubbling in N_2 gas and by a short period of pumping. Cl_2 gas was then bubbled in until the solution turned yellow. (Time required was about 15 minutes.) The volatiles were removed by pumping, leaving a white solid. The nmr spectrum of this solid,dissolved in CH_2Cl_2, showed a six-peak multiplet centered at 175 Hz,downfield from internal TMS, with intensity ratios of approximately 1:12:15:15:12:1. The infrared spectrum showed both N-H stretch (3200 cm^{-1}) and N-D stretch (2400 cm^{-1}), but the N-D stretch was five to six times as intense. Thus the product was a mixture of $(CH_3)_2NHBCl_3$ and $(CH_3)_2NDBCl_3$ in a ratio of 1:6.

Reaction of N-deuterodimethylamine-dichloroborane and chlorine. -- A solution of $(CH_3)_2NDBHCl_2$ was prepared as described above, the excess HCl gas having been removed by bubbling in N_2 gas and by a short period of pumping. Cl_2 gas was then bubbled in until the solution turned yellow. (Time required was about 5 minutes.) The volatiles were removed by pumping, leaving a white solid. The nmr spectrum of this solid,dissolved in CH_2Cl_2 showed a six-peak multiplet centered at 175 Hz,downfield from internal TMS, with intensity ratios of approximately 1:20:25:25:20:1. The infrared spectrum showed both N-H stretch (3200 cm^{-1}) and N-D stretch (2400 cm^{-1}), but the N-D stretch was seven to eight times as intense. Thus the product was a mixture of $(CH_3)_2NHBCl_3$ and $(CH_3)_2NDBCl_3$ in a ratio of 1:8.

Reaction of N-deuterodimethylamine-borane and chlorine at low temperature. -- A sample of $(CH_3)_2NDBH_3$ (about 0.05 g) was dissolved in 10 ml of CH_2Cl_2 and the solution cooled to about -78° by immersion in a dry ice/acetone bath. Cl_2 gas was bubbled into the solution for 10 minutes at which time the solution was yellow. The volatiles were removed by pumping, leaving a white solid. The nmr spectrum of this solution showed a quartet, centered at 175.5 Hz, downfield from internal TMS, with intensity ratio of approximately 1:1.2:1.2:1. Two very low-intensity satellite peaks were visible, one upfield and one downfield of the quartet, in positions corresponding to the 1st and 6th peaks of the $(CH_3)_2NHBCl_3$ sextet. The infrared spectrum of this solid showed both N-H stretch (3200 cm^{-1}) and N-D stretch (2400 cm^{-1}), but the N-D peak was fifteen to twenty times as intense as the N-H peak. Thus the product is a mixture of $(CH_3)_2NHBCl_3$ and $(CH_3)_2NDBCl_3$ in a ratio of approximately 1:20.

Reaction of N-deuterodimethylamine-trichloroborane and hydrogen chloride. -- A mixture of $(CH_3)_2NHBCl_3$ and $(CH_3)_2NDBCl_3$ in a ratio of 1:1 was prepared, as described above, by the reaction of $(CH_3)_2NDBH_3$ and Cl_2. A sample of this mixture (about 0.05 g) was dissolved in 25 ml of CH_2Cl_2, and HCl gas was bubbled into the solution for 2 hours. (During this time, the CH_2Cl_2 lost by evaporation was replaced to keep a nearly constant volume of 25 ml.) After the addition of HCl, the volatiles were removed by pumping, leaving a white solid. The nmr spectrum of this solid was superimposable on the nmr spectrum of the starting mixture. The infrared spectrum of this solid was the

same as the infrared spectrum of the starting mixture within the limits of variation expected from variation in pellet composition. Thus $(CH_3)_2NDBCl_3$ and HCl do not exchange to a measurable extent at room temperature within 2 hours.

A mixture of $(CH_3)_2NHBCl_3$ and $(CH_3)_2NDBCl_3$ in a ratio of 1:20 was prepared, as described above, by the reaction of $(CH_3)_2NDBH_3$ and Cl_2 at -78°. A sample of this mixture (0.0170 g) was dissolved in 3 ml of 0.12 M HCl in CH_2Cl_2. The ratio of HCl:adduct was thus approximately 3:1. About 1 ml of the resulting solution was transferred into an nmr tube, and the nmr spectrum was monitored as a function of time. There was no observable change in the spectrum, even after 24 days. Therefore, within the limits of detectability of nmr, HCl does not exchange with $(CH_3)_2NDBCl_3$ within 24 days.

<u>Reaction of N-deuterodimethylamine-trichloroborane with hydrogen chloride and chlorine.</u> -- A sample (about 0.02 g) of nearly pure $(CH_3)_2NDBCl_3$ prepared, as described above, by the reaction of $(CH_3)_2NDBH_3$ and Cl_2 at -78°, was dissolved in 15 ml of CH_2Cl_2, and both HCl gas and Cl_2 gas were bubbled into the solution for 30 minutes. The volatiles were then pumped off, leaving a white solid. The nmr spectrum of this solid was superimposable on the nmr spectrum of the starting material. The infrared spectrum of this solid was the same as the infrared spectrum of the starting material within the limits of variation expected from variation in pellet composition. Thus $(CH_3)_2NDBCl_3$ and HCl do not exchange to a measurable extent at room temperature in the presence of Cl_2 within 30 minutes.

Reaction of dimethylamine-trichloroborane and deuterium chloride. -- Dimethylamine-trichloroborane (0.0353 g, 0.218 mmol) was dissolved in 1 ml of a 0.22 M solution of DCl in CH_2Cl_2 in an nmr tube, and the nmr spectrum was monitored as a function of time. There was no observable change in the spectrum, even after 11 days. Therefore, within the limits of detectability of nmr, DCl does not exchange with $(CH_3)_2NHBCl_3$ within 11 days.

Table I

Infrared Data for Some Amine-Haloboranes[a]

$(CH_3)_2NHBF_3$:	3260(m), 3080-2960(m), 1630-1600(w), 1465(m), 1340(m), [1150, 1040, 940, 910(s)], 705(w), 560(w), 480(w).
$(CH_3)_2NHBCl_3$:	3180(s), 3020(w), 2970(w), 2780(w), 2700(w), 2660(w), 2440(w), [1475, 1465, 1450, 1440(m)], 1410(m), 1380(m), 1340(m), 1230(w), 1195(w), [1150, 1140, 1130(m)], 1050(w), 1010(m), 900(s), 840(m), 810(s), 780-700(s), 510(m), 460(w), 375(w), 360(m).
$(CH_3)_2NHBBr_3$:	3220(m), 3150(s), 2780(w), 2680(w), [1470, 1460, 1445, 1435(m)], 1410(m), 1370(m), 1335(m), 1200(w), [1140, 1130(m)], 1000(m), 895(s), 825(m), 790(s), [710, 680, 665(s)], 455(m).
$(CH_3)_2NHBI_3$:	3300-2950(s), 2770(m), 2640(w), 1500-1430(s), 1405(m), 1360(m), 1330(m), 1200(m), [1135, 1125(m)], 1040(w), 1015(w), 990(m), 895(m), 820-790(m), 775(m), [645, 620, 600(s)], 550(w), 420(m).
$(CH_3CH_2)NHBH_2Cl$:	3190(s), 3040(sh), 2990(s), 2945(w), 2910(w), 2890(w), 2840(w), 2450(s), 2370(m), 1470(m), 1445(m), 1395(m), 1370(w), 1315(w), 1260(m), 1190(m), 1150(s), 1130(s), 1100(m), 1065(m), 1030(m), 1020(sh), 980(w), 870(m), 790(m), 710(w), 615(m).

Table I (continued)

$(CH_3CH_2)NHBH_2I$:	3140(s), 2990(s), 2980(s), 2940(w), 2500(s), 2450(s), 1465(m), 1450(m), 1420(w), 1390(m), 1360(w), 1250(m), 1180(m), 1130(s), 1110(s), 1050(s), 1025(s), 1005(s), 885(m), 865(m), 810(w), 790(m), 760(w), 700(w).
$(CH_3CH_2)NHBHCl_2$:	3200(s), 2990(s), 2950(m), 2500(s), 1460(s), 1400(s), 1290(sh), 1265(m), [1175(w), 1140(s), 1115(sh), 1070(m), 1025(s)], 910(m), 880(m), 810(sh), 790(m), 745(m), 680(s), 545(m), 520(m).
$(CH_3CH_2)NHBCl_3$:	3190(s), 2970(s), 1470(s), 1450(sh), 1370(s), 1290(s), 1260(m), 1170(m), 1125(m), 1095(s), 1060(m), 1030(m), 1010(m), 910(m), 870(s), 830(m), [780(s), 740(s), 710(s)], 560(s), 460(w).
$(CH_3CH_2)NHBBr_3$:	3200(sh), 3160(s), 2990(sh), 2960(s), 2940(sh), 1465(m), 1445(m), 1390(m), 1375(m), 1300(w), 1285(m), 1255(w), 1190(w), 1165(w), 1120(w), 1090(s), 1055(m), 1020(m), 1005(m), 900(w), 875(sh), 870(s), 820(w), 770(s), 700(w), 665(s), 645(s), 520(s), 450(w).

[a] All values are in cm^{-1}. Symbols: s = strong, m = medium, w = weak, sh = shoulder.

Table II

^{1}H NMR Data for $(CH_3)_2NH$ and $(CH_3)_3N$ Adducts

Borane	$(CH_3)_2NH$ Adducts			$(CH_3)_3N$ Adducts	
	δ_{CH_3} [a]	J_{HNCH} [b]	J_{BNCH} [b]	δ_{CH_3} [a]	J_{BNCH} [b]
BH_3	152.0	5.5	----	155	----
BH_2Cl	156.0	5.5	----	158	----
BH_2Br	161.5	5.5	----	163	----
BH_2I	165.5	5.5	----	169	----
$BHCl_2$	162.0	5.5	----	163	----
$BHBr_2$	168.5	5.5	----	174	----
BHI_2	173.5	5.5	----	183	----
BF_3	155	5.8	1.9	157	1.6 [c]
BCl_3	175	5.8	2.9	178	2.7
BBr_3	182	5.4	3.4	188	3.1
BI_3	189	5.2	3.7	199	3.4

[a] In Hz, downfield from internal TMS.

[b] In Hz,

[c] $J_{FBNCH} = 0.8$ Hz.

Table III

^1H NMR Data for $(CH_3CH_2)_3N$ Adducts

Borane	$\delta^a_{CH_3}$	$\delta^a_{CH_2}$	$J^b_{H_3CCH_2}$	J^b_{BNCH}
BH_3	69.5	165.5	7.4	----
BH_2Cl	69.5	173.0	7.1	----
BH_2Br	69.5	176.5	7.0	----
BH_2I	70.0	179.5	7.0	----
$BHCl_2$	76.5	185.5	7.2	----
$BHBr_2$	78.0	197.5	7.3	----
BHI_2	79.5	201.5	7.3	----
BF_3	72.5	176.5	7.0	$<2.0^c$
BCl_3	82.0	203.0	7.3	2.6
BBr_3	87.0	214.5	7.3	2.8

[a] In Hz, downfield from internal TMS.

[b] In Hz.

[c] $J_{FBNCH} < 1.0$ Hz.

Table IV

^{1}H NMR Data for $(CH_3CH_2)_2NH$ Adducts

Borane	δ_{CH_3} [a]	δ_{CH_2}(avg) [a]	δ_{NH} [a,d]	CH_2(A) $\delta_{CH_2(A)}$ [a]	CH_2(A) $J_{HNCH_2(A)}$ [b]	CH_2(A) $J_{H_3CCH_2(A)}$ [b]	J_{AB} [b]	CH_2(B) $\delta_{CH_2(B)}$ [a]	CH_2(B) $J_{HNCH_2(B)}$ [b]	CH_2(B) $J_{H_3CCH_2(B)}$ [b]
BH_3	74.0	168.0	230	168.0	7.0	7.2	-----	168.0	7.0	7.2
BH_2Cl	75.3	179.0	255	184.3	5.3	7.3	-13.0	173.7	5.7	7.4
BH_2Br	76.4	183.3	250	189.2	4.3	7.3	-12.9	177.3	5.7	7.2
BH_2I	77.2	185.3	250	189.1	4.8	7.2	-13.4	181.4	5.5	7.4
$BHCl_2$	80.1	192.2	250	200.8	4.8	7.2	-13.2	182.6	-0.5	7.2
$BHBr_2$	82.4	196.7	265	205.1	4.6	7.2	-13.1	188.2	-0.5	7.1
BHI_2	83.3	196.5	250	210.8	4.1	7.2	-13.2	182.8	-0.2	7.1
BF_3	76.0	181.5	240	----[c]	---[c]	7.3	----[c]	----[c]	---[c]	7.3
BCl_3	85.6	202.0	---	224.6[d]	4.6[d]	7.5	-13.2[d]	187.3[d]	-0.2[d]	7.5
BBr_3	88.9	211.3	---	235.7[d]	4.6[d]	7.4	-13.2[d]	187.8[d]	-0.2[d]	7.4

[a] In Hz, downfield from internal TMS.

[b] In Hz.

[c] Multiplet structure not resolved; values not determinable.

[d] Poor resolution; approximate values are given.

CHAPTER IV

DISCUSSION

Halogenation of Amine-Boranes

As noted earlier, the procedures involved in the halogenation of trimethylamine- and pyridine-boranes were developed by M. A. Mathur and V. R. Miller, among others.[24,25,50-52] In this work these procedures have been extended to include the synthesis of haloborane adducts of dimethylamine, diethylamine, and triethylamine. In so doing, some general trends in reactivity have become apparent, which seem to be consistent with the existence of a steric effect on reactivity.

The fact that trimethylamine-borane and the pyridine-boranes showed differences in reactivity was noted by Mathur,[25] and these differences were attributed to an involvement of the aromatic ring in stabilizing the boron during the halogenation of pyridine-borane. However, in this work it has been observed that the reactivity of secondary amine-boranes parallels that of pyridine-boranes. Some examples of these differences in reactivity are enumerated below:

1) When HCl is allowed to react with R_3NBH_3, the reaction stops at monochlorination. When HCl is allowed to react with R_2NHBH_3 or with $C_5H_5NBH_3$, the reaction does not stop at monochlorination, but proceeds to dichlorination.

2) The reaction of I_2 with R_3NBH_3 requires elevated temperature (around 110°) or a relatively long exposure time to produce

diiodinated products. The reaction of I_2 with R_2NHBH_3 or with $C_5H_5NBH_3$ proceeds smoothly and relatively rapidly to diiodinated product without reflux. It is important to note also that more I_2 is required to diiodinate R_3NBH_3 than is required to diiodinate R_2NHBH_3 or $C_5H_5NBH_3$:

a) $R_3NBH_3 + 3/2X_2 \rightarrow R_3NBHX_2 + 1/2H_2 + HX$

b) $\begin{matrix} R_2NHBH_3 \\ \text{or} \\ C_5H_5NBH_3 \end{matrix} + X_2 \rightarrow \begin{matrix} R_2NHBHX_2 \\ \text{or} \\ C_5H_5NBHX_2 \end{matrix} + H_2$

The relative stoichiometries imply that HI will diiodinate R_2NHBH_3 or $C_5H_5NBH_3$ but not R_3NBH_3.

3) The haloborane adducts of trimethylamine are not particularly sensitive to hydrolysis. The haloborane adducts of secondary amines or pyridine are much less stable towards hydrolysis.

If one looks for a feature common to both the secondary amines and the pyridine, relative to tertiary amines, one sees that both secondary amines and pyridines have less steric bulk than tertiary amines. The greater reactivity of secondary amine-boranes and pyridine-boranes, relative to tertiary amine-boranes, may be due, therefore, to the fact that there is less steric hindrance to reaction in the former systems.

Steric effects on reactivity are not limited to just the differences in bulk of the amines. There also appears to be an effect which parallels the trends in the bulk of the halogen, or halogenating agent. The most obvious examples of this sort of reactivity differences are given below:

1) The reaction of Cl_2 with any of these amine-boranes proceeds to trichlorinated product with no difficulty. On the other hand, I_2 requires heat and/or long exposure times to fully iodinate these amine-boranes.

2) The reaction of Cl_2 with the secondary amine-boranes produces mixtures of products at all stages of reaction, whereas the reaction of Br_2 with the secondary amine-boranes produces nearly pure dibrominated product before any tribrominated product is observed. This implies that the reaction of Cl_2 with the intermediate products is not significantly slower than the reaction of Cl_2 with the starting borane. In contrast, the reaction of Br_2 with the intermediate product $R_2NHBHBr_2$ is markedly slower than the reaction of Br_2 with R_2NHBH_2Br. The reaction of I_2 with secondary amine-boranes gives clean product at each step, implying that the reaction of I_2 with R_2NHBH_2I is markedly slower than with R_2NHBH_3, yet significantly faster than with R_2NHBHI_2.

The last point illustrates a general trend, namely that reaction to further halogenate an amine-borane is slower the more halogens there are already substituted on boron. That is, the order of reactivity towards halogenating agents is:

$$\text{AmineBH}_3 > \text{AmineBH}_2\text{X} > \text{AmineBHX}_2 .$$

It is highly probable that this trend in reactivity arises from the increase

in steric hindrance due to the bulky halogen groups on boron. There are a few halogenating agents, such as Cl_2, which are so powerful that these differences in reactivity are minimized to the point that at all intermediate stages of reaction, mixtures of products result.

In one case, an unusual combination of effects is observed. Exhaustive iodination of dimethylamine-borane or trimethylamine-borane produces triiodinated product. Attempts to exhaustively iodinate diethylamine-borane or triethylamine-borane produce, after diiodinated product, ammonium salts. In this case, the combination of bulky ethyl groups and bulky iodine apparently results in the cleavage of the B-N bond concomitantly with reaction of the diiodinated product with iodine.

Reaction of Dimethylamine and Boron Trihalides

The classical method of synthesis of amine-trihaloboranes involves the direct addition of the amine to the boron trihalide.[64,65] The reaction of a tertiary amine with a boron trihalide produces, in good yield and purity, the amine-trihaloborane. In an attempt to prepare aminoboranes, Brown[58] reacted dimethylamine with boron trichloride, added triethylamine to the product, and isolated in good yield dimethylaminodichloroborane and triethylamine hydrochloride. Brown identified the intermediate product as dimethylamine-boron trichloride on the basis of one chloride analysis. In a similar manner, Goubeau[66] reacted dimethylamine with boron tribromide, added triethylamine to the product, and isolated in good yield dimethylamino-dibromoborane and triethylamine hydrobromide. He stated that the intermediate product was dimethylamine-tribromoborane but offered no basis for that

identification. Goubeau attempted to prepare dimethylamine-boron trichloride by two methods. In the first case, he reacted dimethylamine with boron trichloride and isolated a product by sublimination in vacuum. This product gave a good analysis for dimethylamine-boron trichloride but was still impure, even though sublimed. In the second case, he reacted hydrogen chloride with dimethylaminodichloroborane and isolated a pure compound with properties similar to trimethylamine-boron trichloride, but no other identification was given.

The first quantitative examination of the reaction between secondary amines and boron trihalide was reported by Gerrard,[56] who examined the reaction of several secondary amines with boron trichloride. It was determined that side products were formed in considerable quantity in all cases and that the ratio of various products formed was dependent on the conditions of reaction, especially the solvent used and the organic substituent on the amine. The equation below (not balanced) shows the products observed:

$$R_2NH + BX_3 \rightarrow R_2NHBX_3 + R_2NH_2^{+}BX_4^{-} + R_2NBX_2 + (R_2NH)_2BX_2^{+}BX_4^{-} \ (?)$$

In the case of dimethylamine reacting with boron trichloride, Gerrard reported the isolation of the 1:1 adduct, dimethylammonium tetrachloroborate, and dimethylaminodichloroborane. However, infrared evidence was mentioned for another product, bis-(dimethylamine)-dichloroboronium tetrachloroborate, and the data account for only 2/3 of the starting material. Also it was proposed that the 1:1 adduct was ionic, namely, $(CH_3)_2NHBCl_2^{+}Cl^{-}$, which proposal conflicts with the evidence obtained by Goubeau[66] on the same

compound prepared by addition of hydrogen chloride to dimethylamino-dichloroborane. In summary, Gerrard served notice that the direct reaction of secondary amines with trihaloboranes did not yield pure adducts, but it was not yet clear just what the products were.

It is noteworthy that this present work gives the first detailed report of the preparation of the dimethylamine adducts of boron trichloride, boron tribromide, or boron triiodide, free of impurities.

The preparation of the dimethylamine adduct of boron trifluoride has been reported elsewhere;[57,58] these reports were confirmed in this present work. This is the only dimethylamine-trihaloborane adduct which is produced free of impurities by the reaction of dimethylamine and the boron trihalide. There is, however, some evidence for side reactions, even in this system. If $(CH_3)_2NH$ is in excess in the reaction of $(CH_3)_2NH$ and BF_3, the nmr signal observed for the adduct collapses to a 1:1:1:1 quartet (J = about 2 Hz), and a singlet appears upfield, the chemical shift corresponding to $(CH_3)_2NH_2^+$. The lack of coupling in the peak due to $(CH_3)_2NH_2^+$ implies an equilibrium exists, as shown in the equation below:

$$(CH_3)_2NHBF_3 + (CH_3)_2NH \rightleftarrows (CH_3)_2NBF_3^- + (CH_3)_2NH_2^+$$

This sort of reactivity has been examined by Ronan and Gilje.[67] The septet pattern of the adduct is restored when more BF_3 is introduced. Excess BF_3 has no effect on the septet pattern; therefore, reaction to produce BF_4^- and $(CH_3)_2NHBF_2^+$ does not occur. If the reaction did occur, the septet pattern should collapse to a doublet.[68]

The reactions of dimethylamine with boron trichloride and with boron tribromide were examined in detail in this present work. These reactions are discussed in the paragraphs which follow.

The first step in the reaction of dimethylamine with a boron trihalide is certainly adduct formation. Kistiakowsky[69] has shown for several cases that adduct formation proceeds with little or no activation energy. However, once the adduct is formed, several reactions can occur, for example:

1) Proton abstraction by $(CH_3)_2NH$:

$$(CH_3)_2NHBX_3 + (CH_3)_2NH \rightarrow \begin{array}{c} (CH_3)_2NBX_3^- + (CH_3)_2NH_2^+ \\ \text{or} \\ (CH_3)_2NBX_2 + (CH_3)_2NH_2^+X^-, \end{array}$$

following which, reaction with BX_3 would yield:

$$\begin{array}{c} (CH_3)_2NBX_3^- + (CH_3)_2NH_2^+ \\ \text{or} \\ (CH_3)_2NBX_2 + (CH_3)_2NH_2^+X^- \end{array} + BX_3 \rightarrow (CH_3)_2NBX_2 + (CH_3)_2NH_2^+BX_4^-.$$

The overall equation is given below:

$$2(CH_3)_2NH + 2BX_3 \rightarrow (CH_3)_2NBX_2 + (CH_3)_2NH_2^+BX_4^-.$$

2) Displacement of X^- by $(CH_3)_2NH$:

$$(CH_3)_2NHBX_3 + (CH_3)_2NH \rightarrow [(CH_3)_2NH]_2BX_2^+X^-,$$

following which, reaction with BX_3 would yield:

$$[(CH_3)_2NH]_2BX_2^+X^- + BX_3 \rightarrow [(CH_3)_2NH]_2BX_2^+BX_4^-.$$

The overall equation is given below:

$$2(CH_3)_2NH + 2BX_3 \rightarrow [(CH_3)_2NH]_2BX_2^+BX_4^-.$$

3) Halide abstraction by BX_3:

$$(CH_3)_2NHBX_3 + BX_3 \rightarrow (CH_3)_2NHBX_2^+BX_4^-,$$

following which, reaction with $(CH_3)_2NH$ would yield either:

$$(CH_3)_2NHBX_2^+BX_4^- + (CH_3)_2NH \rightarrow [(CH_3)_2NH]_2BX_2^+BX_4^-,$$

or:

$$(CH_3)_2NHBX_2^+BX_4^- + (CH_3)_2NH \rightarrow (CH_3)_2NBX_2 + (CH_3)_2NH_2^+BX_4^-.$$

The overall equations are given below:

a) $2(CH_3)_2NH + 2BX_3 \rightarrow [(CH_3)_2NH]_2BX_2^+BX_4^-$;

b) $2(CH_3)_2NH + 2BX_3 \rightarrow (CH_3)_2NBX_2 + (CH_3)_2NH_2^+BX_4^-$.

There are, of course, a variety of alternative reactions which could be written, but all would be derived from these three, and with one exception all would result in the same side products. (The exception is that bis- or trisaminoboranes might be produced according to the following reaction sequence:

$$R_2NBX_2 + R_2NH \rightarrow R_2NBX_2 \cdot NHR_2 \xrightarrow{R_2NH} (R_2N)_2BX + R_2NH_2^+X^- \xrightarrow{BX_3} (R_2N)_2BX + R_2NH_2^+BX_4^-;$$

$$(R_2N)_2BX + R_2NH \rightarrow (R_2N)_2BX \cdot NHR_2 \xrightarrow{R_2NH} (R_2N)_3B + R_2NH_2^+X^- \xrightarrow{BX_3} (R_2N)_3B + R_2NH_2^+BX_4^-.)$$

It is important to note that in the three reaction schemes shown above, the reaction products for each scheme have a net stoichiometry of $1(CH_3)_2NH$: $1BX_3$, which is the same as the 1:1 adduct. Therefore, elemental analysis of the reaction mixture will <u>not</u> distinguish between possible reaction paths; only a complete product analysis will allow one to comment on the reaction path.

An examination of the products of the reaction of dimethylamine with boron trichloride or boron tribromide shows clearly that either sequence 2) or sequence 3-a) is being followed in these systems after initial adduct formation, since the product analysis showed the product mixture to contain principally the adduct and bis-(dimethylamine)-dihaloboronium tetrahaloborate salts. The other sequences would require the product mixture to contain ammonium salts and aminoboranes.

In light of the reaction of $(CH_3)_2NHBF_3$ with excess $(CH_3)_2NH$, which is certainly a proton abstraction reaction, it is surprising that proton abstraction is not observed to occur to any great extent in these systems. It is quite likely that experimental conditions play a role in determining reaction stoichiometry; thus under different conditions the proton abstraction route might be more favored. Nevertheless, it has been established in other work in this laboratory that halide displacement by amine[70,71] or halide abstraction by a Lewis acid[68] <u>is</u> a facile route to boron cations.

It should be noted that the infrared data do not require that BX_4^- be the only anion formed in the reactions which lead to ionic products. It is quite probable that some X^- is present, and in the case of X = Br, the experimental results (the observation of BBr_3 in the volatiles) require the presence of considerable quantities of Br^-.

Finally, there remained the possibility that the cation could be formed directly from the adduct without reaction with excess amine or BX_3. This was suggested by a recent report, in which Nöth[72] reported the synthesis of $(CH_3)_2NHBCl_3$ by direct reaction of $(CH_3)_2NH$ and BCl_3 and the subsequent

isolation of $[(CH_3)_2NH]_2BCl_2^+Cl^-$ in 74% yield as the result of refluxing that "$(CH_3)_2NHBCl_3$" for 7 hours in Et_2O. (Another product was $Et_2O \cdot BCl_3$.) Our data show a near 70% yield of $[(CH_3)_2NH]_2BCl_2^+BCl_4^-$ as the result of addition of $(CH_3)_2NH$ to BCl_3. To test what happens with authentic $(CH_3)_2NHBCl_3$, a sample (0.28 g) was refluxed in 30 ml of Et_2O for 8 hours. A small amount of white solid in the solution was filtered off (0.016 g, 6%). An infrared spectrum of the solid was very similar to that of $[(CH_3)_2NH]_2BCl_2^+$ BCl_4^-. The Et_2O was evaporated from the solution to give, after transfer to a tared vial, 0.23 g (82%) of a solid whose infrared and nmr check for $(CH_3)_2NHBCl_3$ (a small amount of aminoborane was present, as indicated by nmr, but this was much less than 5% of the fraction).

In another experiment a sample of authentic $(CH_3)_2NHBCl_3$ (0.27 g) was dissolved in 40 ml of C_6H_6, heated at 40-50° for 6 hours, and then refluxed for 1 hour. A very small amount of solid precipitated during the reflux, but not enough for any analysis. The benzene was evaporated from the solution to give, after transfer to a tared vial, 0.19 g (71%) of a white solid whose infrared and nmr check for $(CH_3)_2NHBCl_3$.

These data clearly show that Nöth's report[72] was in error. The data indicate that what Nöth called $(CH_3)_2NHBCl_3$ was probably a mixture of adduct and boronium salt whose composition was not appreciably affected by refluxing in Et_2O.

In summary, the direct reaction of dimethylamine and boron trichloride or bromide results in the formation of bis-(dimethylamine)-dihaloboronium tetrahaloborate salts along with the expected adducts. To obtain pure adducts,

one may take advantage of the low solubility of the boronium salts, or one may directly halogenate dimethylamine-borane.

Reaction of N-Deuterodimethylamine-Borane with Various Halogenating Agents

The initial nmr results from the diethylamine-haloboranes were quite unexpected. The nmr signals for the methylene protons in mono- or dihaloborane adducts of diethylamine were not a doublet of quartets as expected on a first order basis, but were instead complex multiplets containing many more than eight lines. The nmr spectra of the two trihaloborane adducts of diethylamine were more complex yet. In an attempt to simplify the spectral pattern, N-deuterodiethylamine-borane was prepared (in a manner exactly analogous to that described in the experimental section for the preparation of N-deuterodimethylamine-borane*) and used as the starting material for several halogenation reactions. It was expected that the deuterium atom in place of the proton on nitrogen would not couple to the methylene protons, and would thus produce a simplified pattern for those protons. However, the patterns were not any less complex,** and indeed the infrared spectra of the trichloroborane adduct thus prepared clearly showed the presence of both N-H and N-D bonds. This indicated that some exchange had taken place in the course of reaction. Some qualitative experiments

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* IUPAC - approved name is dimethylamine (ND)-borane.[73]

** It should be noted that the complex pattern observed for the methylene protons of the two expected products $(CH_3CH_2)_2NDBH_2I$ and $(CH_3CH_2)_2NDBHI_2$ were exactly that which one would predict for the pattern of $(CH_3CH_2)_2NHBH_2I$ and $(CH_3CH_2)_2NHBHI_2$, if all coupling constants between the proton on nitrogen and the methylene protons were set equal to zero.

were performed which seemed to indicate that the extent of exchange of N-H for N-D as the result of chlorination of $(CH_3CH_2)_2NDBH_3$ by Cl_2 was unaffected by added HCl, nor was the product affected by exposure to HCl or DCl. However, the system was analyzable only by means of the infrared spectra since the nmr spectra were much too complex. Accordingly, a thorough examination of the analogous dimethylamine system was performed, as described in the experimental section.

The following facts stand out as the principal results of these experiments:

a) At -78° HCl does not exchange with $(CH_3)_2NDBH_3$, $(CH_3)_2NDBH_2Cl$, or $(CH_3)_2NDBHCl_2$.

b) HCl alone does not exchange with $(CH_3)_2NDBH_2Cl$ or $(CH_3)_2NDBHCl_2$ within a half-hour at room temperature.

c) Exchange and chlorination both result from the reaction of HCl and $(CH_3)_2NDBH_3$. Therefore, it is not known whether HCl will exchange with $(CH_3)_2NDBH_3$ without reaction occuring.

d) HCl, even with Cl_2, does not exchange with $(CH_3)_2NDBCl_3$ within a half-hour at room temperature.

e) $(CH_3)_2NDBCl_3$ and HCl do not exchange within 24 days at room temperature. $(CH_3)_2NHBCl_3$ and DCl do not exchange within 11 days at room temperature.

f) During the reaction of $(CH_3)_2NDBH_3$, $(CH_3)_2NDBH_2Cl$, or $(CH_3)_2NDBHCl_2$ with Cl_2, exchange occurs. In the case of $(CH_3)_2NDBH_3$, exchange occurs even at -78°, although the extent of exchange is much less than at room temperature.

g) The addition of HCl in large excess during the reaction of $(CH_3)_2NDBH_3$ and Cl_2 has no noticeable effect on the extent of exchange, while the addition of DCl in large excess during the same reaction markedly reduces the extent of exchange of H for D on nitrogen.

h) Bromination of $(CH_3)_2NDBH_3$ to the tribromoborane adduct with Br_2 is accompanied by very little exchange. Iodination with I_2 to the mono- or diiodoborane adduct does not induce exchange at all.

Several plausible mechanisms could be proposed for this exchange process; however, only one mechanism appears to be consistent with all the facts.

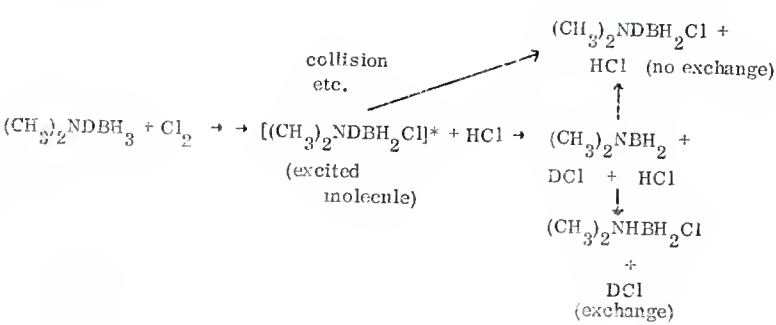
The idea that direct exchange between an N-D bond and an HCl molecule might be the principal mechanism is certainly attractive, but if it were, the addition of excess HCl to the system $(CH_3)_2NDBH_3 + Cl_2$ should have increased the extent of hydrogen incorporation, whereas in fact it had no effect at all[g) above].

A mechanism requiring that exchange only occur on $(CH_3)_2NDBH_3$ before any reaction takes place to produce halogenated amine-borane is also attractive, but the fact that significant exchange is observed during the reactions of $(CH_3)_2NDBH_2Cl$ or $(CH_3)_2NDBHCl_2$ with Cl_2 [f) above] effectively disproves the postulation.

Conversely, any mechanism involving exchange only after all halogenation reactions are over is disproved by the fact that HCl does not exchange with $(CH_3)_2NDBCl_3$, even with Cl_2 present, within the time limits of the reactions [d) above].

It would not be incorrect to assume that, during the first step of reaction of $(CH_3)_2NDBH_3$ and Cl_2, direct exchange could occur between HCl and unreacted $(CH_3)_2NDBH_3$. As evidenced by the reaction of D_2O and $(CH_3)_2NHBH_3$ to produce $(CH_3)_2NDBH_3$, exchange may occur at nitrogen in the presence of an acidic group, and HCl would certainly qualify. However, as soon as an amine-borane is chlorinated, HCl alone can no longer cause exchange if the molecule is at room temperature, yet exchange does occur in the presence of Cl_2. Since the function of Cl_2 is to chlorinate the amine-borane, it would seem reasonable to conclude that the chlorination process momentarily "activates" the molecule for exchange.

The one mechanism which appears to be consistent with all the facts involves the loss of DX from an activated (or "hot") molecule still in an excited vibrational state as the result of halogenation, thus producing an aminoborane as an intermediate. If the aminoborane picks up HX, present in the solution as a product of the halogenation reactions taking place, then exchange occurs. If it picks up DX again, no net exchange occurs. The stepwise equations for this mechanism for the first step of chlorination are shown below:



The mechanism would suggest that if chlorination occurs at room temperature, nearly all of the excited molecules produced would have the energy required to undergo loss of DCl, but that most of the molecules would quickly dissipate that energy by collision or some other thermal path. Thus in the presence of a certain minimum amount of HCl, the extent of exchange would be determined almost entirely by the probability that an excited molecule will dissipate its excess energy through the loss of DCl. In other words, the addition of excess HCl would have little effect on the ratio of H to D in the product. On the other hand, addition of excess DCl would tend to sweep out all of the HCl produced by reaction, leaving very little HCl for exchange, thus reducing the amount of H incorporated into the product.

Note that this mechanism requires that the intermediate aminoborane have a lifetime sufficiently long so as to allow escape of DCl from the solvent cage. Otherwise, the aminoborane would simply re-add DCl, and no net exchange would have taken place.

The mechanism would also suggest that the energy imparted to the amine-borane as a result of bromination is less than that imparted as a result of chlorination, so that the chances are lower that a brominated molecule would have sufficient energy to allow it to undergo loss of DBr. Iodination would impart still less energy so that no exchange occurs at all. These ideas are reasonable when one recalls that Cl_2 is a much more powerful halogenating agent than Br_2, and Br_2 more powerful than I_2.

Two points concerning this mechanism deserve further comment. The first point is that the idea of a "hot" molecule as the key intermediate requires

not only a reactive step which is very energetic but also one which isolates (or concentrates) the energy of reaction in a B-X bond for a finite period of time. A concerted process (as opposed to a radical process, for which precedence exists in systems of this sort) would not concentrate the energy effectively since the energy of reaction would be distributed over at least two bonds and would also be released in kinetic energy of more than one molecule. Thus this mechanism would seem to require a radical process for the halogenation reactions.

A second and related point is the fact that although on statistical grounds, one would predict more exchange would occur when more than one Cl is on boron, one actually finds less exchange occurring. The rationalization which seems the most reasonable is that the energy isolated in one B-Cl bond at the moment of reaction is quickly distributed over other B-Cl bonds if they exist. This is reasonable because the B-Cl motions would be highly coupled to each other when more than one Cl is attached to boron. Therefore, the first halogenation step would give the most exchange because the energy would remain concentrated in one B-Cl bond for a longer period of time.

It is interesting to note that one can determine the more thermodynamically favored products of these exchange processes by taking into account the changes in zero-point energy* as a result of exchange:

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* Zero-point energy is the energy of vibration possessed by a molecule in its lowest vibrational energy state.

Bond	$\bar{\nu}$ (cm^{-1})
N-H	3100* (3200**)
Cl-H	2885*
Br-H	2560*
I-H	2230*
N-D	2160† (2400‡)
Cl-D	2050† (2090*)
Br-D	1810†
I-D	1540†

From the data above one can calculate the change in zero-point energy for the process, $R_1R_2R_3ND + HX \rightarrow R_1R_2R_3NH + DX$, by first determining the change in frequency, $\Delta\bar{\nu}$, for the process and converting the change in frequency to a change in energy, ΔE, by use of the equation, $\Delta E = 1/2\, hc\Delta\bar{\nu}$, where $h = 6.625 \times 10^{-27}$ erg-sec, $c = 2.998 \times 10^{10}$ cm/sec, and 1.00 erg = 1.44×10^{16} cal/mole. The results of this calculation are given below:

X	$\Delta\nu$ (for ND + HX → NH + DX)	ΔE (cal/mole)
Cl	105 cm^{-1}	150
Br	190	270
I	250	355

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* Values taken from reference 74.

† Calculated from the equation $\bar{\nu}_{YH} = \sqrt{2}\,\bar{\nu}_{YD}$.

** Observed in this work for $(CH_3)_2NHBCl_3$.

‡ Observed in this work for $(CH_3)_2NDBCl_3$.

If one assumes that entropy effects for these reactions are negligible* and that the ΔE values calculated above correspond to enthalpy changes,† then, since $\Delta G = \Delta H - T\Delta S$, it follows that for these systems, $\Delta G = \Delta E$. Now since ΔE is positive in all three cases, the reactions to produce N-H and DX from N-D and HX are not favorable. That is, the thermodynamically favored products are N-D and HX.

At this point one may calculate equilibrium constants for these systems (as shown below):

$$R_2NDBX_3 + HX \rightleftarrows R_2NHBX_3 + DX,$$

making no more assumptions than those made above. The equation used to calculate the equilibrium constants is:

$$\log K = -\Delta E/2.303RT$$

where $R = 1.987$ cal/mole-°K and T = absolute temperature. The results of the calculation are given below:

X	K
Cl	0.776
Br	0.634
I	0.550

Unfortunately, attempts to verify these values failed, because the systems do not apparently have a mechanism available for achieving equilibrium [e) above].

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* This is reasonable since there is no change in the number or type of molecules.

† This is reasonable since there is no change in volume associated with the process.

General ^{1}H NMR Results

There can be no question as to the place of nuclear magnetic resonance in chemistry today. Nmr has become one of the most powerful tools available for studying a wide variety of chemical systems, including such diverse problems as reaction kinetics, structure, product yields, product identification, and reaction mechanisms. However, in spite of its usefulness, there is still considerable controversy in the literature concerning the origin of chemical shifts.

The ^{1}H nmr data for the haloborane adducts of dimetbyl- and trimetbylamine are given in Table II, and are shown graphically in Figure 32. It is clear that substitution of halogen (Cl, Br, or I) for hydrogen in these amine-boranes produces a downfield sbift of the resonance of the methyl groups. It is also clear that this downfield shift is larger the larger the halogen introduced or the greater the number of halogens introduced. It is significant that the bulkier amine, trimethylamine, shows a greater downfield shift for a given change in borane substituents than does the less hindered dimethylamine. There is no a priori reason for this difference if the shift is determined solely by an inductive mechanism because tbe two amines are nearly the same in base strength. It is therefore proposed that the greater steric interaction between the halogens and the nitrogen substituents in the trimethylamine adducts results in a greater downfield shift for the methyl protons in the trimethylamine-haloboranes. It is also significant that the trifluoroborane adducts show almost no change in chemical shift from that of

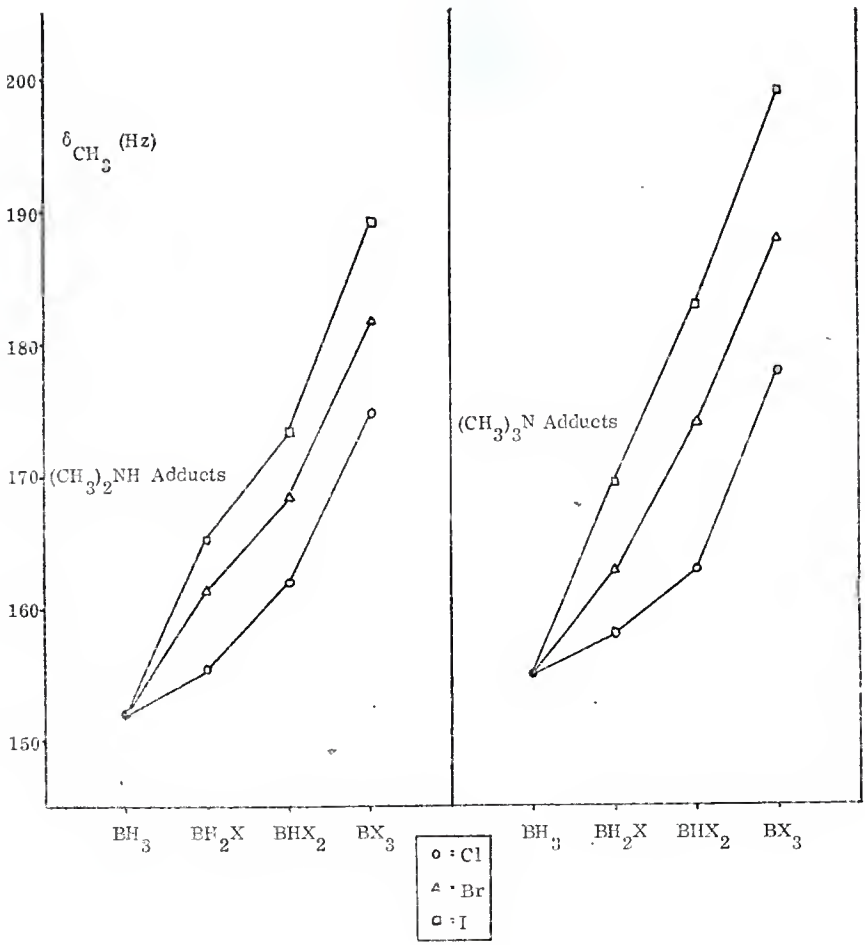


Figure 32. Chemical shift of methyl protons in haloborane adducts of $(CH_3)_2NH$ and $(CH_3)_3N$ as a function of extent of halogen substitution on boron.

the BH_3 adducts. Little or no steric interaction would be expected in these cases. (In other work in this laboratory, chemical shifts have been determined for mono- and disubstituted fluoro-[75] and oxo-[76] borane adducts of trimethylamine. In these cases, small upfield shifts from the borane are noted, probably caused by the anisotropic effects of the B-O and B-F bonds.)

Tables III and IV give the ^1H nmr data for the haloborane adducts of triethyl- and diethylamine, respectively. These data are displayed graphically in Figure 33. From this figure it is again clear that the substitution of a halogen (Cl, Br, or I) for hydrogen in an amine-borane results in a downfield shift of the resonances due to protons in alkyl groups in the amine. The relative changes in chemical shift for the methylene protons in these ethylamine-boranes are greater than for the methyl protons in the methylamine-boranes mentioned above. The order of steric bulk, as indicated by these chemical shift changes is:

$$(CH_3)_2NH < (CH_3)_3N < (CH_3CH_2)_2NH < (CH_3CH_2)_3N,$$

which order would have been expected.

It is interesting to note the effect of substitution on the chemical shift of terminal methyl groups in the adducts of the two ethylamines. Monohalogenation has almost no effect at all, dihalogenation produces moderate downfield shifts, and trihalogenation causes larger shifts yet. This indicates increasing interaction between borane halogens and these methyl groups, which is consistent with this model, since such interactions should be minimal with only one halogen on boron but of increased importance with two or three halogens on boron. A consideration of space models suggests that the

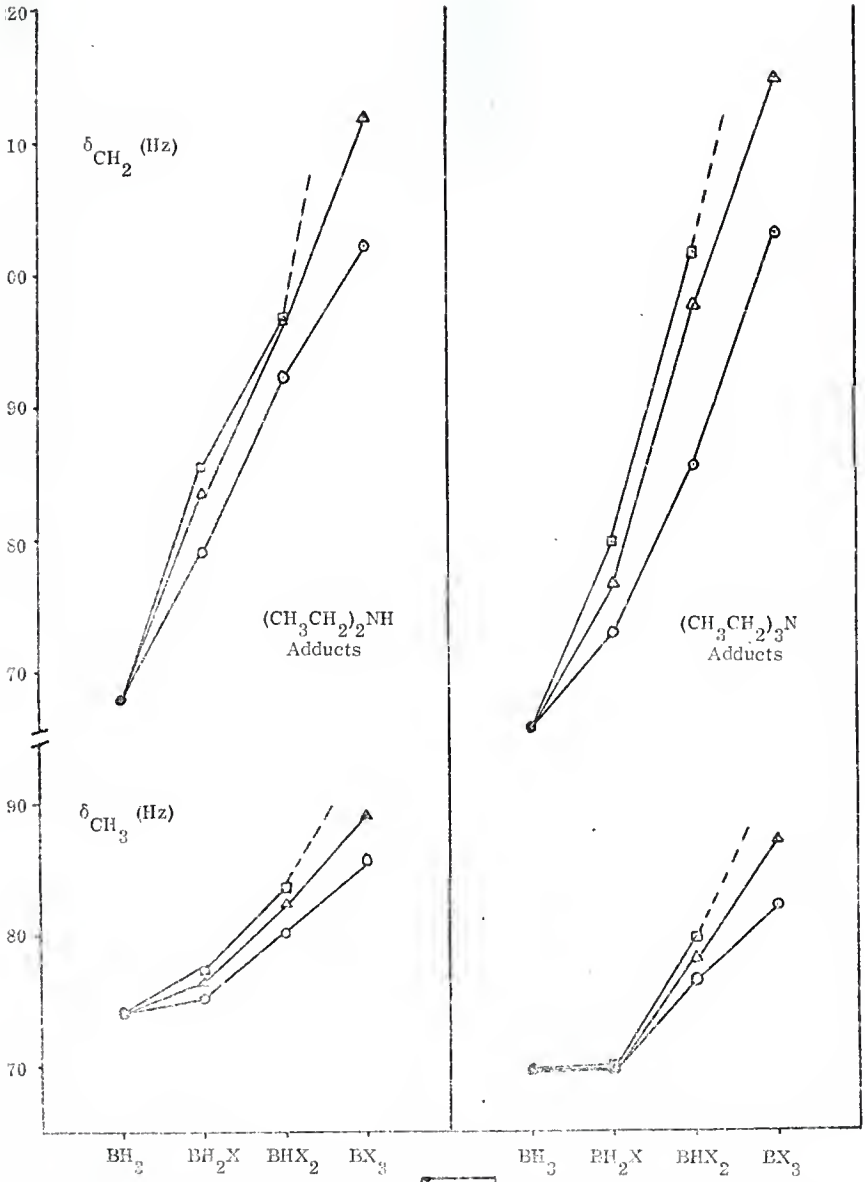


Figure 33. Chemical shift of methyl and methylene protons in haloborane adducts of $(CH_3CH_2)_2NH$ and $(CH_3CH_2)_3N$ as a function of extent of halogen substitution on boron.

methyl groups are easily able to move out of the way of one halogen on boron but not two or three.

Possible Explanations of the Effect of Boron-Attached Halogens on the NMR Shifts of Alkyl Protons in Donor Groups Attached to Boron

For the particular systems under discussion here (namely halogenated amine-boranes) the chemical shift has been shown to parallel the steric interaction between halogens on boron and protons in alkyl groups in donors coordinated to boron. In particular, the effect is a downfield shift upon substitution of halogens for hydrogen in an amine-borane, the shift being greater the more halogens substituted or the larger the halogens are.

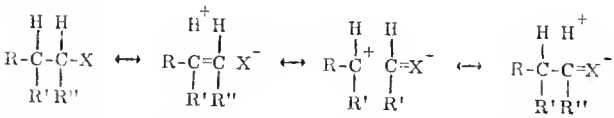
There are several possible explanations for this phenomenon, all of which certainly contribute to the overall effect, though probably not to the same degree. These include:

1) Intramolecular van der Waals' forces between halogens and the alkyl protons.
2) Magnetic anisotropy around the halogen, in the boron-halogen bond, or in the boron-nitrogen bond.
3) Magnetic anisotropy in C-C or C-N bonds adjacent to the C-H bonds, which is induced in some undefined manner by the presence of the boron atom.

Our analysis of the system strongly favors the first explanation, but we cannot completely rule out the other two with the information available.

Studies on proton shielding in haloalkanes (systems analogous to those under discussion here) have been carried out by several groups. Although the

systems studied did not have the steric interference of our systems, the conclusions reached are enlightening as to the factors to be considered. Bothner-by and Naar-Colin[77] concluded that factors other than electronegativity were at work in determining shifts of groups more than one carbon away from the halogen. No hard conclusions were reached, but the suggestion was made that either mesomeric effects or long-range bond anisotropy effects may be the cause of the observed shifts. The mesomeric effect would be best explained as an increase in the contribution of resonance forms which, through π-bonding effects, increase the electron density of the halogen, as shown below:



The larger the halogen, the more forms II, III, and IV would contribute. This effect would be greatly attenuated (as should a purely inductive effect) by the interposing bonds between the halogen and the proton in the amine-borane systems.

The overall effect of bond anisotropy was found to be a combiuation of two factors, one producing a paramagnetic effect, the other a diamagnetic effect, and in practice, the two effects partially cancel one another. The more ionic the carbon-halogen bond becomes, the more the paramagnetic term diminishes; thus, for a C-Cl bond, the effect is principally a result of electronegativity, while for a C-I bond, the diamagnetic anisotropy predominates. (The relative contribution of these factors is apparently affected by the structure

of the rest of the molecule.) It should be pointed out that in the equation used to calculate the quantitative effect, a term for the distance between the anisotropic bond and the affected proton entered as an inverse cube, implying that this effect would be sensitive to small changes in distance.

The same authors mentioned that the shielding of the protons α to halogen correlated very well with the dipole moment of the molecule; thus the effect of the halogens may be to polarize the C-H bonds as a result of the total molecular dipole moment, which would certainly be largely determined by the halogens.

Cavanaugh and Dailey[78,79] discussed the shielding effects in the same compounds, but reached different conclusions. They concluded that there is a contribution to the chemical shift due to the presence of C-C bonds adjacent to the affected proton, in addition to a contribution as a result of inductive withdrawing of electron density by halogens. The chemical shift was viewed as arising from a linear combination of these two effects, and the effect at positions α, β, and γ to the halogen was evaluated. Thus, comparing two compounds:

$$X\text{-}CH_2\text{-}CH_3 \qquad \text{and} \qquad X\text{-}CH(CH_3)_2$$

(I) (II)

the chemical shifts of the α protons in these two compounds are different because there are different numbers of C-C bonds in the two cases:

$$\delta^{*}(\alpha H\text{-I}) = \delta^{\dagger}(\text{elect. of X at } \alpha H) + \delta^{**}(C\text{-}C)$$

$$\delta(\alpha H\text{-II}) = \delta(\text{elect. of X at } \alpha H) + 2\delta(C\text{-}C)$$

However, the chemical shifts of the β protons are about the same, since there is only one C-C bond adjacent to each β proton:

$$\delta(\beta H\text{-I}) = \delta(\text{elect. of X at } \beta H) + \delta(C\text{-}C)$$

$$\delta(\beta H\text{-II}) = \delta(\text{elect. of X at } \beta H) + \delta(C\text{-}C).$$

This sort of correlation worked very well for a wide variety of substituents:

$$X = Cl, Br, I, OH, CN, COOH, C_6H_5, -O-, -S-, CHO, NH_2, NO_3, -S_2-.$$

The question of the origin of this C-C bond shift was not answered in this study. The idea that it could be a purely anisotropic effect seemed to the authors to be incorrect since anisotropy played such a small role in determining the shifts of the methyl derivative, and since the magnitude of the effect is so large for the ethyl and propyl derivatives. It should be noted that the magnitude of the C-C bond shift was found to be proportional to the size of the substituent, which implies a steric origin for the effect.

Spiesecke and Schneider[80] examined both ^{1}H and ^{13}C nmr shifts of a series of CH_3X and CH_2CH_2X compounds. It was concluded that the major contributions to these shifts came from the inductive and magnetic anisotropy effects of the X substituent. (The comment was made that these results contradict the conclusions of Cavenaugh and Dailey.[79]) It was also noted by Spiesecke and

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* δ(αH-I) is the chemical shift of the protons α to the group X in compound I.

† δ(elect. of X at αH) is the contribution to the chemical shift of a proton due to the electronegativity of the group X at a position α to the proton.

** δ(C-C) is the contribution to the chemical shift of a proton due to the presence of a C-C bond on the same carbon as the proton.

Schneider that even their conclusions were not complete, since several aspects of the problem remained inadequately explained. The presence of an as yet uncharacterized contribution to the chemical shift was suggested as the explanation for these aspects.

Schaeffer, Reynolds, and Yonemoto[81] brought a fresh viewpoint to the problem and came the closest to suggesting a reasonable explanation applicable to the system under discussion in this work. It was pointed out that two factors disfavor anisotropy playing a major role in determining chemical shifts in alkyl halides. One factor is that the equation relating anisotropy to shielding effects (based on the point-dipole approximation of McConnell[82]) is not valid in cases where the radius of the charge distribution giving rise to the anisotropy is of the same order of magnitude as the distance between the point-dipole and the point of interest. The second factor is that in the case of these alkyl halides, the experimental observations are in many cases opposite to what would be predicted on the basis of anisotropic effects. In particular, an upfield shift is predicted for several cases where a downfield shift is actually observed.

Schaeffer, et al. resolved this quandry by invoking shifts due to van der Waals' interactions. Citing the work of Buckingham, Schaeffer, and Schneider[83] on dispersion forces in intermolecular solvent effects, these authors pointed out that a downfield shift is expected from each of two types of interaction:

i) Interaction in the equilibrium configuration causes a distortion of the electron cloud surrounding the nucleus, which distortion is probably an expansion.

2) The motion of the molecules at moderate temperatures leads to a time-dependent distortion of the symmetry of the C-H bonds. For molecules whose C-H bonds are exposed to a "sideways" attack, this effect could become important.

The first type of interaction is possible if the molecule is at all crowded, and the second could arise from internal rotations and vibrations of the molecule. These effects should increase as the number of electrons in the preturbing atom increases. That is, the effect should be greater for the larger halogens.

Haigh, Palmer, and Semple[84] expanded on this idea by observing that three factors involving intramolecular van der Waals' forces contribute to the determining of chemical shifts (much of the argument is derived from the work of Marshall and Pople[85]):

1) At all ranges, London dispersion forces polarize the atoms' electron clouds towards each other (according to an inverse sixth-power law), reducing the diamagnetic term, i.e., shifting the absorption downfield.

2) For ranges a little above or below the conventional van der Waals' separation, the repulsive overlap forces produce an opposite effect.

3) At very short range, the major interference of the electron clouds hinders precession and thus produces a downfield shift.

Clearly in severely hindered cases, the third factor will predominate. Experimental evidence has been presented in several cases to support this contention. Nagata, Terasawa, and Tori[86] reported observing the deshielding of protons as a result of steric interference by other proximate hydrogen atoms.

The degree of deshielding was found to be closely related to the distance between the interfering protons. Winstein, Carter, Anet, and Bourn[87, 88] reported on the effects of steric compression on chemical shifts and coupling constants in half-cage and related molecules. These systems involved steric interaction between an OH group (or $-O^-$) and a proton in another part of the molecule. Large downfield shifts were again noted, the larger shifts noted for the more sterically crowded system.

In the system under discussion in the present work, there is certainly tremendous steric interaction between the protons in the alkyl portion of the molecule and the halogens attached to boron. Taylor's X-ray work[12] confirms this, as does a consideration of approximate bond lengths, bond angles and van der Waals' radii for an H-C-N-B-X system, as shown in Figure 34.

Thus, the nmr results obtained in this work reflect the great steric strain inherent in these systems. Other effects such as magnetic anisotropy are not of sufficient magnitude to be important in determining the net chemical shifts of these compounds.

The only other reasonable explanation for the trend in chemical shifts of these compounds is Onyszchuk's inductive argument. This argument is effectively destroyed by the results obtained from the study of the nmr spectra of the diethylamine-haloboranes, as discussed in detail in the section which follows this section. The fact that such a large non-equivalence exists between two protons the same number of bonds away from boron cannot be rationalized on the basis of an inductive effect transmitted through the bonds.

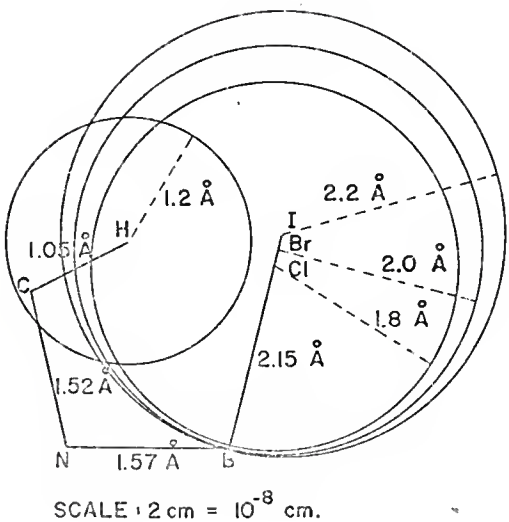


Figure 34. Sketch of approximate bond lengths, bond angles, and van der Waals' radii for an H-C-N-B-X system (X = Cl, Br, I) showing the potential for severe overcrowding.

Such an effect must of necessity affect the two protons to the same extent. The data are, however, easily and reasonably explained on the basis of steric interference resulting in a downfield shift, which shift increases with the severity of the interference.

It must be noted that the proposal of a relationship between nmr shifts and steric factors does not require a relationship between those steric factors and net stability of the molecules involved. In other words, the assertion that steric interactions between halogens on boron and alkyl groups on nitrogen increase with increasing size or number of halogens does not assert that this increase in steric interaction is accompanied by a concomitant destabilizing of the adduct (or, more correctly, of the B-N bond), since other factors may increase the bond strength. Indeed, one only has to compare the gas-phase dissociation data of Onyszchuk[8] with the X-ray work of Taylor,[12] both concerning the trimethylamine-haloboranes. Onyszchuk showed clearly that boron tribromide forms the most stable adduct, boron trichloride next, and boron trifluoride the weakest. Taylor showed that the B-N bond lengths in the BBr_3 and BCl_3 adducts were, within experimental error, the same. One must conclude, therefore, that the bond length is determined by a combination of bonding strength and steric repulsion, both of which increase from the BCl_3 to the BBr_3 adduct, so that the bond length is not changed significantly. Had the increase in steric repulsion caused a decrease in the B-N bond strength, the B-N bond length in the BBr_3 adduct should have been considerably longer than in the BCl_3 adduct. Had there been no increase in steric repulsion, the

increase in B-N bond strength should have caused the B-N bond in the BBr_3 adduct to be considerably shorter than in the BCl_3 adduct.

Diethylamine-Haloborane ^1H NMR Results

The pattern of the ^1H nmr resonance observed for the methylene (CH_2) protons of the diethylamine-haloborane adducts is not a simple doublet of quartets, as one might predict on a first order basis. Instead the pattern observed is extremely complex, due to the non-equivalence of the two methylene protons. These spectra were analyzed as the AB portion of an $ABCD_3$ spectrum using a computer program, as described in the procedures section. The results of these analyses are given in Table IV and are shown graphically in Figure 35. That the methylene protons of these adducts should be non-equivalent is not surprising. Magnetic non-equivalence of this sort is possible in any system in which a methylene group is attached to a tetrahedral center with three different groups on it. [This is illustrated in Figure 36, in which Newman projections are shown for 1) RCH_2CXYZ and 2) $CH_3CH_2N(H)(Et)(BXY_2)$, where Et = CH_2CH_3, and X, Y = H, Cl, Br, I.] Depending on the differences in size among the three groups, different amounts of non-equivalence may arise as the result of two effects:[89-91]

1) Intrinsic non-equivalence - near free rotation but with different torsional preferences for similar positions of the methylene protons. This corresponds to a rotational potential energy curve which has minima in energy which occur at positions other than at 60° dihedral angles and which has relatively small differences in energy between maxima and minima.

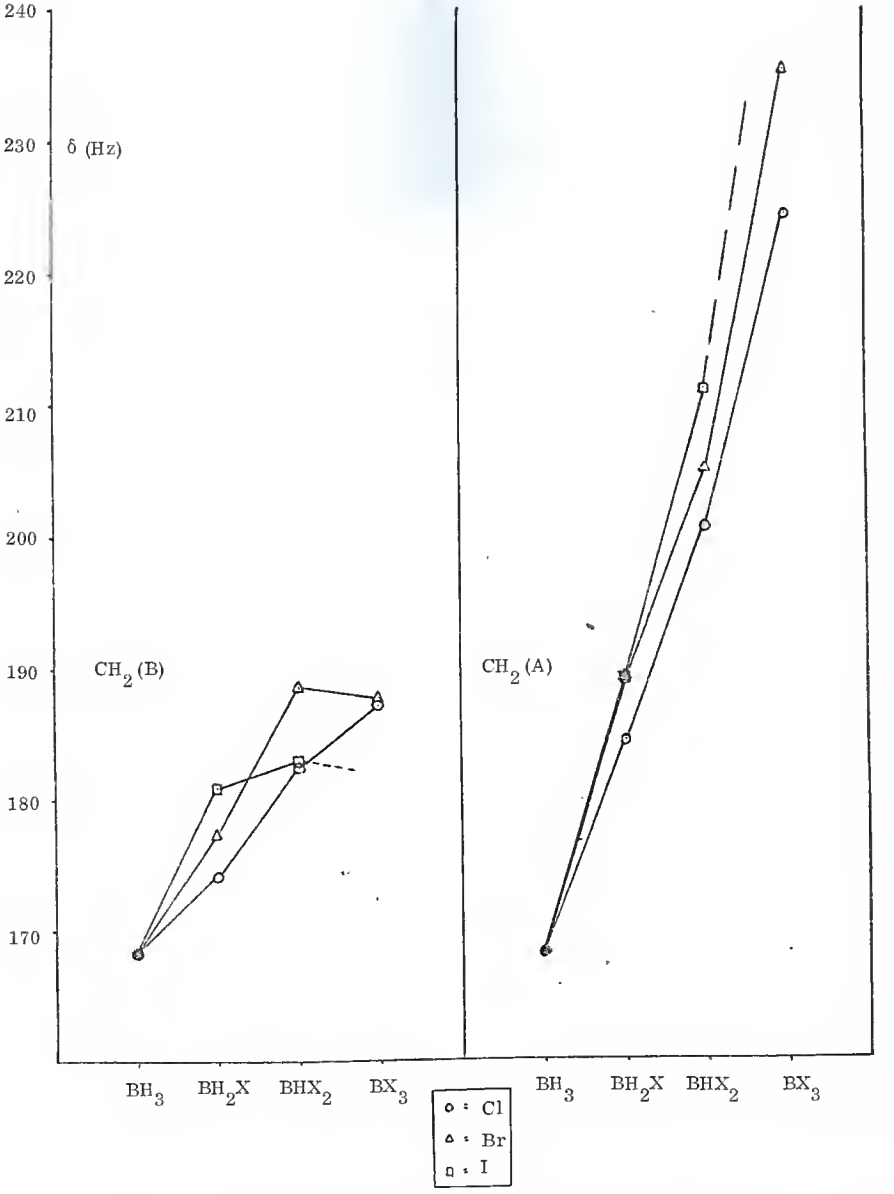
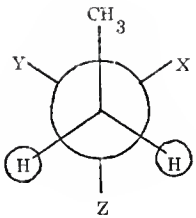


Figure 35. Chemical shift of non-equivalent methylene protons in haloborane adducts of $(CH_3CH_2)_2NH$ as a function of extent of halogen substitution on boron.



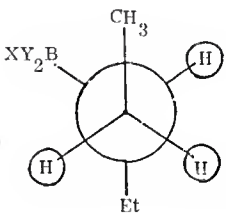


Figure 36. Newman projections showing similarity between CH_3CH_2CXYZ and $CH_3CH_2N(H)(Et)(BXY_2)$.

2) Non-equal conformer population - the relative rotation population is such as to make one (or two) rotation(s) favored over the other(s). This corresponds to a rotational potential energy curve which has one (or two) minimum (a) in energy much lower in energy than the other(s) and which has relatively large differences in energy between maxima and minima.

Non-equivalence of methylene protons in a borane system has been observed in two instances; however, in neither case was the resulting pattern analyzed. Coyle and Stone[34] observed a complicated methylene spectrum for $(CH_3CH_2)_2SBH_3$, which they attributed to non-equivalence of the methylene protons; in this case, the lone pair of electrons on the sulfur acted as a stereochemically significant group. Rothgery and Hohnstedt[92] observed an AB pattern for the methylene protons between nitrogen and the carbonyl group in $CH_3CH_2OC(O)CH_2NH(CH_3)\cdot BX_3$ (X = H, Cl). Additional comments on their work will be made in a later section.

The values for δ_{CH_2} for the diethylamine-haloborane adducts, as shown in Figure 33, are averages of the values for the two non-equivalent protons. Figure 35 shows graphically the actual values for the chemical shifts of these non-equivalent protons. (Using standard notation, the downfield proton is labelled proton A and the upfield proton, proton B.) Examination of Figure 35 shows that proton A is extremely sensitive to halogen substitution on boron, while proton B is relatively insensitive. This implies that proton A is, on the average, very close to the borane moiety, while proton B is insulated from

it. (The anomalous changes in the shift of proton B between BH_2I and BHI_2 and between $BHBr_2$ and BBr_3 are significant. More will be said about this later.)

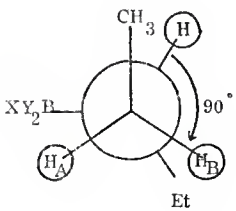
At this point it is possible to establish more definite information concerning preferred rotational conformers by considering, in addition to chemical shifts, the changes in the coupling constants between the nitrogen-attached proton and the two methylene protons, as a function of substitution on boron (Table IV). The values for $J_{HNCH(A)}$ are in the range 4.5 to 5.5 Hz for all the adducts. On the other hand, the values for $J_{HNCH(B)}$ drop to about zero when more than one halogen is substituted on boron. The Karplus rule for ethane-type systems[93] predicts that $J_{HCCH'}$ will be at a minimum when the dihedral angle, Φ, between the two protons is 90°:

$$J = J^0 \cos^2 \Phi + C \qquad [0^\circ \leq \Phi \leq 90^\circ]$$

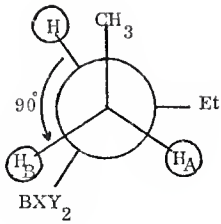
$$J = J^{180} \cos^2 \Phi + C \qquad [90^\circ \leq \Phi \leq 180^\circ]$$

(J^0, J^{180}, and C are constants; J^0 and J^{180} are the coupling constants for $\Phi = 0^\circ$ and 180°, respectively, and C is the coupling constant for $\Phi = 90^\circ$. Typically $J^0 \approx J^{180} \approx$ 5-10 Hz and $C \approx 0$ Hz.) The coupling constants observed in our system imply, then, that when more than one halogen is substituted on boron in diethylamine-borane, one rotamer is strongly preferred, and that this rotamer has a dihedral angle between the N-H bond and the C-H(B) bond of about 90°.

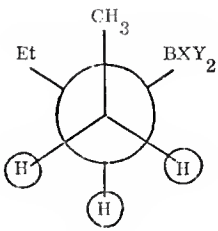
The three possible rotamers for this system are shown, as Newman projections looking down one C-N bond, in Figure 37. [Rotamers I and II are shown torsionally twisted by interaction between the methyl group and the



A



B



C

Figure 37. Newman projections showing rotameric isomers of $(CH_3CH_2)_2NHBXY_2$ (with torsional preferences).

nearest hulky group on nitrogen. Protons A and B are labelled according to dihedral angle, proton B being 90° (dihedrally) from the N-H group.] Rotamer III is ruled out because it has the bulky methyl group between the two hulky groups on nitrogen. Rotamer II is ruled out because it would require that proton B he more sensitive to halogen substitution on boron. Rotamer I is the preferred rotamer since it has a dihedral angle of about 90° hetween the N-H bond and the C-H(B) bond, and since it has proton A near and proton B well-insulated from the borane moiety.

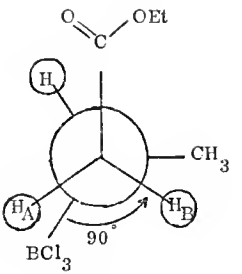
Recall now the anomalous changes in the chemical shift of proton B between BH_2I and BHI_2 and hetween $BHBr_2$ and BBr_3. The fact that proton B is totally insensitive to the new halogen substituted on boron implies that this is the point at which rotamer I is nearly completely "frozen out." Thus it takes one iodide or two hromides to freeze the rotation, but even with three chlorides, there is still some freedom of rotation. This trend is perfectly in line with the trends in steric bulk of the halogens.

Further Comments

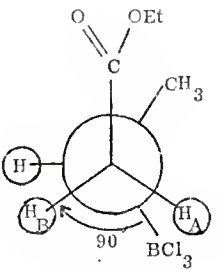
Comments on the Work of Rothgery and Hohnstedt

It is interesting to apply the sort of viewpoint developed in this present work to the observations of Rothgery and Hohnstedt[92] on non-equivalent methylene protons in borane adducts of amino acid esters. In particular, the compound $CH_3CH_2OC(O)CH_2N(H)(CH_3)\cdot BCl_3$ shows non-equivalence of the methylene protons between the nitrogen and the carhonyl group. An examination of the nmr spectrum of this compound, as recorded in Figure 2

of this reference, shows $J_{HNCH(A)} \approx J_{HNCH(B)} \approx 8Hz$, $J_{BNCH(A)} \approx 4Hz$, and $J_{BNCH(B)} \approx 0Hz$, where CH(A) and CH(B) are downfield and upfield, respectively. The zero value of $J_{BNCH(B)}$ strongly suggests some sort of preferred rotameric population distribution. If one assumes that a Karplus-type relationship exists for boron coupling to hydrogen across three bonds, then these observations require that there be a $\sim 90^\circ$ dihedral angle between boron and CH(B) in the preferred rotamer, and,secondly, that this preferred rotamer be much more favored than other rotamers, since large contributions of other rotamers would cause the average $J_{BNCH(B)}$ to be non-zero. In addition, the near equal J_{NHCH} values require that this rotamer not have a 90° dihedral angle between N-H and either CH_2. Additionally, the magnitude of the value suggests that the nitrogen proton is not between the two CH_2 protons, since if it were, the two dihedral angles would be expected to be equal (i.e., 60°) for the values to be equal, and the maximum value of J predicted for a dihedral angle of 60° would, by analogy to carbon systems, be about 6 Hz. Finally, since proximity to borane has been shown by our work to cause downfield shifts, the greater shift arising from the greater proximity, the proton which is farther away from boron is the proton which must have a dihedral angle to boron of 90°. This requires that the boron be between the two protons, 90° from one and 30° from the other. This leaves two possible rotameric forms (A and B in Figure 38). Rotamer A can be ruled out since the 90° dihedral angle between boron and CH(B) would require a 90° dihedral angle between N-H and CH(A), which means $J_{HNCH(A)}$ would be zero. Rotamer B on the



A



B

Figure 38. Newman projections of two rotameric forms of $CH_3CH_2OC(O)CH_2N(H)(CH_3)\cdot BCl_3$.

other hand has angles between N-H and the two CH_2 protons of 30° (proton A) and 150° (proton B), and the Karplus rule would predict near equal values for these two coupling constants. Rotamer B is thus the preferred rotamer.

It must be pointed out that this deduction is based on an unestablished assumption, and thus the result is not to be taken as surety. Indeed, steric considerations would at first glance lead one to predict that this rotamer is not so favored as the ones which have no bulky groups eclipsing one another. Nevertheless, the ester group is not spherical, and it is possible that in this particular molecule, the group is rotated such that its interaction with the nitrogen-attached proton is more significant than its interaction with the nitrogen-attached methyl group.

Comments on the Solvent Dependence of NMR Spectra of Diethylamine-Haloboranes

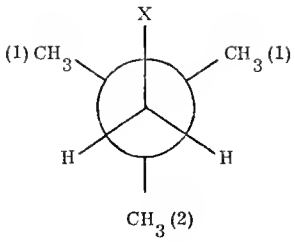
The CH_2 regions of the ^1H nmr spectra of the diethylamine adducts were quite sensitive to changes in solvent. In methylene chloride, the borane (BH_3) adduct showed a 1:4:6:4:1 quintet in the CH_2 region, which is consistent with the CH_2 protons being equivalent, but in benzene solution, the pattern shifted upfield, and showed the complexity associated with non-equivalence. Similarly, on changing from methylene chloride to benzene, the CH_2 region of the spectrum of the dibromoborane ($BHBr_2$) adduct showed a large increase in the shift difference between the two non-equivalent protons, an increase from about 17 to about 40 Hz. These two observations would seem to be most logically explained as follows. Changing from CH_2Cl_2 to benzene as a solvent causes the resonances due to the methylene protons to shift upfield, but the

B proton (the upfield proton in CH_2Cl_2) is shifted farther by this solvent change than is proton A. This implies a specific solvation of one of the two protons,[94] and since the overall shift of both protons is upfield, it would seem reasonable that the more affected proton, proton B, would be the one specifically solvated.

It must be noted that the shifts observed in benzene are due to the large anisotropy associated with the benzene molecule. Indeed the pattern and position of the resonances of these amine-boranes were not appreciably affected by changing from CH_2Cl_2 to solvents such as $CHCl_3$, CCl_4, and CH_3CN.

Comments on the Temperature Dependence of NMR Spectra of Amine-Haloboranes

The work of Kessler[91] on barriers to rotation of tert-butyl groups in organic molecules suggested that in some mono- and disubstituted trimethylamine-boranes, hindered rotation might be observed. If the rate of rotation could be slowed down enough, the methyl groups would become non-equivalent as shown in Figure 39. Accordingly, the nmr spectra of $(CH_3)_3NBHI_2$, $(CH_3)_3NBHBr_2$, and $(CH_3)_3NBH_2I$ were examined at low temperature in CH_2Cl_2 and CS_2. In all cases the signal remained a sharp singlet down to below -80°C. It becomes clear then that the barrier to rotation in these adducts is low; it is probably not low because of a low transition state energy, but rather because of a high ground state energy. In other words, these adducts are so highly hindered that there is little energy difference between staggered and eclipsed forms.



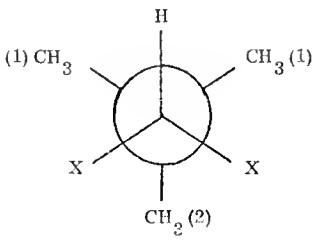


Figure 39. Newman projections showing possible non-equivalence of methyl groups in trimethylamine-haloboranes produced by hindered rotation at low temperature.

The conclusion that there is highly hindered rotation in the diethylamine-haloboranes suggested that at higher temperature this rotation might be more likely to occur freely, thus making the methylene protons in these adducts more nearly equivalent. Accordingly, the methylene region of the spectrum of diethylamine-dibromoborane was examined at temperatures up to about 140° in s-tetrachloroethane. (This solvent was chosen because of its high boiling point, ~149°, and its resemblance to methylene chloride, the solvent for most of this work.) Although the spectrum lost some resolution at higher temperature, probably due to easier relaxation, it did not change in the number or location of peaks. Thus, the methylene region of the spectrum of diethylamine-dibromoborane (in s-tetrachloroethane) is insensitive to increases in temperature. This strongly implies that the molecule is so highly hindered that rotation is not likely to occur, even at 140°.

It should be pointed out that these two conclusions are not inconsistent, though they may at first glance appear to be so. The first case examines rotation about a B-N bond, the nitrogen end of which is highly symmetric. The second case examines rotation about a C-N bond, neither end of which is symmetric. Since the two cases examine rotation about very different types of bonds, the conclusions should be examined separately; that is, the one conclusion has no bearing on the other.

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BIOGRAPHICAL SKETCH

William Howard Myers was born on January 26, 1946, in Oak Ridge, Tennessee, the second of three sons of Dr. and Mrs. Albert L. Myers. He grew up in Jefferson City, Tennessee, graduating from Jefferson High School in May of 1963.

Mr. Myers attended Houston Baptist College in Houston, Texas. He graduated magna cum laude with a B.A. in chemistry in May, 1967. During his college years, Mr. Myers attended special institutes in chemistry at the University of Arkansas, Fayetteville, Arkansas, and at Argonne National Laboratory, Chicago, Illinois.

Mr. Myers entered graduate school at the University of Florida in the fall of 1967, on a National Science Foundation Traineeship. As the result of a problem with the draft, Mr. Myers resigned the NSF traineeship to accept a position as an instructor in the Chemistry Department of the University of Florida for the academic year 1968-69. He was awarded one of five Phillips Petroleum Corporation Teaching Awards for his teaching during this time. Mr. Myers re-entered graduate school at the University of Florida in the summer of 1969, on another NSF traineeship. In the fall of 1969, he was awarded a three-year National Aeronautics and Space Administration Traineeship.

Mr. Myers was commissioned a 2nd Lieutenant in the Chemical Corps of the U.S. Army in June, 1971, as the result of two years' participation in ROTC at the University of Florida.

William Howard Myers is married to the former Barbara Sue McElvany of Houston, Texas. He is a member of the Baptist Church and the American Chemical Society.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Richard D. Dresdner

Richard D. Dresdner
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Zoran R. Pop-Stojanovic

Zoran R. Pop-Stojanovic
Associate Professor of Mathematics

This dissertation was submitted to the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

March, 1972

Dean, Graduate School

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

George E. Ryschkewitsch, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

R. Carl Stoufer
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Merle A. Battiste
Professor of Chemistry

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